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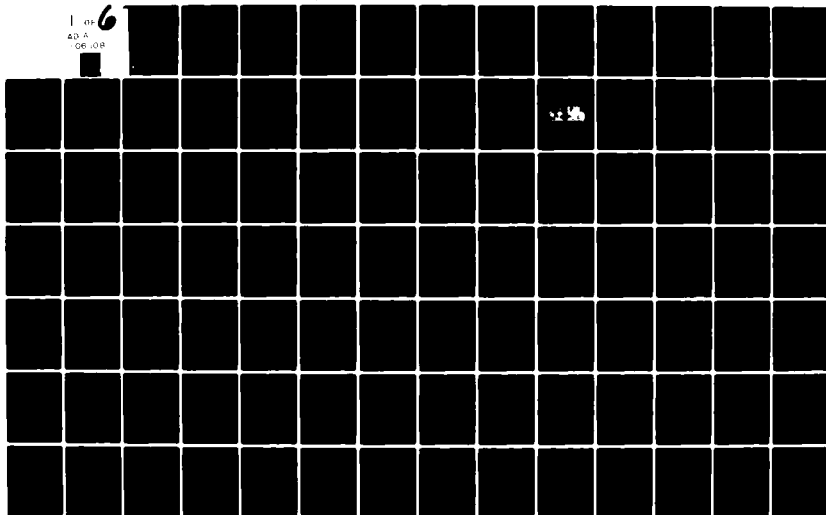
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Twentieth Annual Report

on

MATERIALS RESEARCH

AT

STANFORD UNIVERSITY

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July 1, 1980 - June 30, 1981

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CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY • STANFORD, CALIFORNIA

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Twentieth Annual Report

on

MATERIALS RESEARCH AT STANFORD UNIVERSITY

Information concerning research activities related to the science of materials during the period July 1, 1980 through June 30, 1981.

This research was supported primarily by one or more of the following agencies of the United States Government:

Defense Advanced Research Projects Agency
Department of the Air Force
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Department of Energy
Department of Health, Education and Welfare
Department of the Interior
Department of the Navy
National Aeronautics and Space Administration
National Bureau of Standards
National Science Foundation
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July 1981

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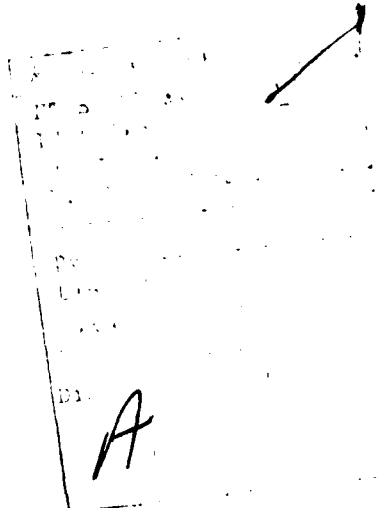
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Science and Engineering
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TABLE OF CONTENTS

	Page
A. INTRODUCTION	1
B. THRUST RESEARCH PROGRAMS	3
1. Nondestructive Testing	
D. Nelson, G. S. Kino, B. A. Auld, G. Herrmann, C. F. Quate, J. C. Shyne, C. R. Steele, A. G. Herrmann	3
2. Polymers	
A. S. Michaels, H. J. Shaw, C. W. Frank, G. G. Fuller, J. G. Linvill, R. S. Feigelson	17
2-a. Photophysics of Amorphous Solid State Polymer Blends: Compatibility and Relaxation Behavior, C. W. Frank	28
2-b. Microrheology of Polymeric Liquids by Two-Color Birefringence, G. G. Fuller	31
3. Novel Catalytic Materials	
R. J. Madix, M. Boudart, W. A. Harrison, W. E. Spicer	32
4. Metastable Materials	
H. C. Andersen, M. R. Beasley, A. I. Bienenstock, T. H. Geballe, A. F. Marshall, R. Sinclair, D. A. Stevenson, G. A. Waychunas	37
4-a. Statistical Mechanics of Glass Formation, H. C. Andersen	39
4-b. Thrust Program on Metastable Materials and Thrust- Related Research, A. I. Bienenstock	40
4-c. Synthesis and Low Temperature Properties of New Materials, T. H. Geballe	46
4-d. Thrust Program on Metastable Materials, A. F. Marshall, R. Sinclair	50
4-e. Thrust Program on Metastable Materials, D. A. Stevenson	53

4-f. Thrust Program on Metastable Materials, G. A. Waychunas	56
5. Metalworking and Plasticity A. K. Miller, D. M. Barnett, E. H. Lee, O. D. Sherby . .	58
C. INDIVIDUAL RESEARCH PROGRAMS	
1. Acoustic and Magnetic Waves and Devices, B. A. Auld . . .	68
2. Deformation in Solids, D. M. Barnett	73
3. Photoelectronic Materials Physics, C. W. Bates, Jr., . . .	76
4. Superconductivity, M. R. Beasley	83
5. Structures of Amorphous Materials and Synchrotron Radiation, A. I. Bienenstock	89
6. Properties of Adsorbents and Catalysts, M. Boudart	92
7. Primary Photochemistry of Photosynthesis, S. G. Boxer . .	96
8. Intrinsic Chemical Reactivity, J. I. Brauman	100
9. Geochemical Studies of Amorphous and Crystalline Silicates, Silicate Melts and Aqueous Solutions, G. E. Brown, Jr.	103
10. Photoelectronic Properties of Solids, R. H. Bube	112
11. Nonlinear Optical Properties and Applications of Single Crystal Fiber LiNbO_3 , R. L. Byer	120
12. Studies in Catalysis, J. P. Collman	123
13. Theoretical Physics of Cooperative Phenomena, S. Doniach	126
14. Theoretical and Experimental Studies in Biophysics, S. Doniach	130
15. Coal Slag Phenomena in Open Cycle MHD Generators, R. H. Eustis	132
16. Experiments at Liquid Helium Temperatures on Macroscopic Quantum Effects, Material Properties, General Relativity, and Superconducting Accelerators, W. M. Fairbank, C. W. F. Everitt, B. Cabrera, H. A. Schwettman	135

17.	Excited State Dynamics and Phonon Effects in Molecular Phases, M. D. Fayer	145
18.	Crystal Synthesis, R. S. Feigelson, D. Elwell, R. K. Route	148
19.	Macromolecular Research, P. J. Flory	157
20.	Photophysics of Polymers in Solution: Energy Transfer and Intramolecular Rotational Diffusion, C. W. Frank	159
21.	Metal Fatigue Studies with Discriminating Specimens, H. O. Fuchs, A. K. Miller, D. V. Nelson	162
22.	Conformation of Adsorbed Polymer Molecules Subjected to Flow, G. G. Fuller	164
23.	Ion Implantation and Laser Annealing of Semiconductors, J. F. Gibbons	166
24.	Mössbauer Effect and Related Phenomena, S. S. Hanna, N. S. Dixon	174
25.	Pseudopotential Methods in Physics, W. A. Harrison	176
26.	High-Resolution and In-Situ Investigations of Small Particles and Reactions on Surfaces, K. Heinemann	179
27.	Physical and Chemical Properties of Interfaces in Silicon Technology, C. R. Helms	186
28.	Electron-Density Approach to Binding Energies of Molecules and Condensed Systems, C. Herring	197
29.	Structural Studies Using Synchrotron Radiation, K. O. Hodgson	199
30.	Solid State Ionics, R. A. Huggins	202
31.	Acoustic Interactions with Solids, G. S. Kino	210
32.	Elastic-Plastic Stress Analysis with Particular Emphasis on Metal-Forming Applications, E. H. Lee	214
33.	Superconductivity and Molecular Physics, W. A. Little	217
34.	Surface Reactivity, R. J. Madix	219
35.	Electrocatalytic Oxidation of Gaseous Hydrocarbons on Solid-Oxide Electrolytes, D. M. Mason	225

36.	Physical Chemistry of Lipid, Lipid-Protein or Lipid-Detergent Bilayer Membranes, H. M. McConnell	227
37.	Deformation and Fracture in Structural Materials, A. K. Miller	235
38.	Multiaxial Fatigue, D. V. Nelson	244
39.	Relations Between Crystalline Imperfections and the Physical Properties of Crystals, W. D. Nix	246
40.	Photon Production from High Energy Electron Beams, R. H. Pantell	253
41.	Physical Chemistry of Oxides and Oxide Surfaces, G. A. Parks	258
42.	Gas-Liquid Metal Reactions and Interactions, N. A. Parlee	261
43.	Electrical, Optical and Metallurgical Properties of Semiconducting Material, G. L. Pearson	267
44.	Electron Beam Technology and Microstructures, R. F. W. Pease	276
45.	Studies of the Dynamics of Molecules and Macromolecules in Liquids, R. Pecora	282
46.	Material Characteristics of Cancellous Bone, R. L. Piziali	286
47.	Computer-Aided Design of Integrated Circuit Fabrication for VLSI Devices, J. D. Plummer	287
48.	Micromechanical Models for the Expansive Process in Expansive Cement Concrete, C. W. Richards	298
49.	Protein Adsorption to Polymer Films, C. R. Robertson	300
50.	Spectroscopy and Quantum Electronics, A. L. Schawlow, T. W. Hansch	302
51.	Interactions of Optical and Acoustic Radiation with Solids, H. J. Shaw	309
52.	Mechanical Behavior of Solids, O. D. Sherby	313
53.	Microstructural Assessment by Acoustic Methods, J. C. Shyne	325

54.	Laser Measurements of Photovoltaic Properties, A. E. Siegman	327
55.	Picosecond Spectroscopy Using a Photoacoustic Detector, A. E. Siegman	329
56.	Measurement of Ultrafast Phenomena, A. E. Siegman	332
57.	Studies of Surfaces and Interfaces in Silicon Based Materials by TEM and AES, R. Sinclair, C. R. Helms	334
58.	Surface, Interface, and Electronic Studies Group, W. E. Spicer, I. Lindau, P. Morgan	339
59.	Solid State Chemistry, D. A. Stevenson	367
60.	Thermophotovoltaic Solar Energy Conversion, R. M. Swanson	374
61.	Ohmic Heterojunction Contacts with Low Interfacial Recombination Velocity, R. M. Swanson	376
62.	Fundamental Aspects of Reactivity in Inorganic Systems, H. Taube	379
63.	Semiconductor Processing, Gas Discharges, Growth- Dissolution and Surface Behavior of Crystals, Biomaterials, W. A. Tiller	383
64.	Solid State Electrochemistry, W. Weppner	392
65.	Development of Implantable Multielectrode Arrays for an Auditory Prosthesis, R. L. White	395
66.	State-to-State Reaction Dynamics, R. N. Zare	396
D.	PUBLICATIONS	399
E.	DOCTORAL DISSERTATIONS	426
APPENDICES		
I.	FACULTY MEMBERS PARTICIPATING IN MATERIALS RESEARCH	431
II.	RESEARCH ASSOCIATES AND PROFESSIONAL STAFF	435
III.	GRADUATE STUDENTS PARTICIPATING IN MATERIALS RESEARCH PROGRAMS	439
IV.	GRADUATE DEGREES CONFERRED	444
V.	NAME INDEX	448

SECTION A

INTRODUCTION

SECTION A

INTRODUCTION

This Twentieth Annual Report includes the total research activity related to the science of materials at Stanford University during the period July 1, 1980 through June 30, 1981. It contains brief descriptions of research programs active during this period.

The report of the research programs is organized into two groupings: (1) the research programs of CMR Members who have participated in one of the five major Thrust group programs supported by the NSF-MRL block grant including their work on the Thrust program and other related research, and (2) individual research programs; when appropriate, members are included in both the Thrust and individual programs. As indicated in their descriptions, some of the research programs were supported by private sources. However, most received support from one or more of the following agencies of the United States government.

- Defense Advanced Research Projects Agency
- Department of the Air Force
- Department of the Army
- Department of Commerce
- Department of Energy
- Department of Health, Education and Welfare
- Department of the Interior
- Department of the Navy
- National Aeronautics and Space Administration
- National Bureau of Standards
- National Science Foundation
- Veterans Administration

The reports of the individual programs are organized by Principal Investigator arranged in alphabetical order, since many programs are cooperative and arrangement by subject would be cumbersome. Also included are compilations of publications, doctoral dissertations, faculty and senior staff members, research associates, graduate students and degrees awarded. Finally, a name index has been added for convenience in locating references to the activities of specific individuals. From this compilation, it can be seen that research on materials and related problems is being conducted within eleven

different academic departments as well as in the Hansen Laboratories.

In addition to the direct support of individual research programs by the agencies mentioned above, broad-base core support was furnished by the National Science Foundation through its Materials Research Laboratory (MRL) Program under Grant No. DMR 77-24222, administered by the Center for Materials Research (CMR), during this past year. Of particular importance has been the financial assistance for the establishment and operation of a group of important central facilities for the synthesis and characterization of new materials.

SECTION B

THRUST RESEARCH PROGRAMS

SECTION B

THRUST RESEARCH PROGRAMS

1. THRUST PROGRAM ON NONDESTRUCTIVE TESTING

G. S. Kino (Coordinator), Professor, Electrical Engineering and, by
Courtesy, Applied Physics
B. A. Auld, Adjunct Professor, Hansen Labs
D. M. Barnett, Professor, Materials Science & Engineering,
Applied Mechanics
A. G. Herrmann, Visiting Associate Professor, Applied Mechanics
G. Herrmann, Professor, Mechanical Engineering, Applied Mechanics,
Civil Engineering
D. V. Nelson, Assistant Professor, Mechanical Engineering
C. F. Quate, Professor, Applied Physics, Electrical Engineering
J. C. Shyne, Professor, Materials Science & Engineering
C. R. Steele, Professor, Mechanical Engineering, Aerophysics and
Astrophysics

Professional Associates:

S. D. Bennett
B. T. Khuri-Yakub

Graduate Students:

R. B. King
M. T. Resch
N. Shaikh
D. Rugar
F. E. Stanke
M. Riazat

Agency Support:

An Associated Program, AFOSR F49620-79-C-0217
An Associated Program, EPRI RP 609-1
NSF-MRL through CMR - Thrust Program on Acoustic Nondestructive
Testing

Technical Objective:

To establish new techniques for nondestructive testing of
materials. We are particularly interested in measurement of stress by
acoustic means and in measurement of stress intensity factor at a
crack. We are also interested in new techniques for measuring the size
and type of macroscopic cracks, microcracks, and flaws, and techniques
for measuring material texture.

Approach:

The measurement of stress in metals by measuring changes in acoustic velocity due to stress, and the measurement of stress intensity factor using this technique and using reflection of acoustic waves from a crack. The development of new techniques for eddy current testing. The development of acoustic microscopy for observation of metal surfaces and integrated circuits.

Research Report:

This interdisciplinary program on nondestructive testing is based on the philosophy that materials and mechanical expertise must be combined with the development of instrumentation to make fundamental progress in the field.

We have been concerned with two basic problems: (1) measuring residual stress and applied stress variations in metals by determining the change in velocity or transit time of an acoustic wave passing through the material; and (2) determining the size and stress intensity factor of cracks in brittle materials and metals by eddy current techniques and by measuring the reflection coefficient of an acoustic wave from a crack. We use these measurements to predict breaking stress of brittle materials and fatigue life of ductile materials.

The acoustic wave stress measurement methods have made good progress during the last year. We now have a fairly well-developed technique using shear waves and a moveable shear wave transducer placed in contact with a metal to determine both the direction and magnitude of shear stress. The work is showing effects of texture, and in particular the small-scale non-uniformities associated with texture in metals. At the same time, longitudinal wave measurements tend to show less criticality to these effects, so that we are obtaining a great deal of insight into the fundamental problems involved in measurements of this kind. The acoustic microscope project has yielded excellent pictures of surface structure of materials.

Work on measuring cracks in glass has been completed. On a separate ONR program similar studies, making use of this background, have been

undertaken to measure cracks in structural ceramics such as silicon nitride. The results are of great importance to the field because they have enabled us to predict breaking stresses due to surface cracks in such materials and to carry out measurements of residual stress and plasticity associated with cracks. These confirm some theoretical predictions of these effects and indicate effects of crack closure and annealing which were not necessarily expected. On the present program, the technique is now being used to measure fatigue cracks in metals and is enabling us, for the first time, to make direct surface acoustic wave measurements on the growth of fatigue cracks while they are being formed in a stressing rig. We believe that this is an important new technique which will provide a great deal of insight into the microcrack formation regime in the early stages of fatigue.

The work on electromagnetic flaw detection in insulating and poorly conducting materials has now been concluded. Small surface pits in silicon nitride samples could be detected by the capacitor probes that have been developed. Good theoretical insight into their operation has been obtained.

Two new projects were begun during the last year. The first was the development of surface acoustic wave techniques for measuring residual stress in materials. Initially, this made use of the contacting Hertzian probe developed for shear waves. Encouraging results were initially obtained, but reproducibility was not easy. Hence, the project was abandoned. Instead, a laser probe non-contacting technique has been developed and appears to be far more reliable and flexible than the earlier technique.

As an extension of the fatigue microcrack measurement methods, a new study project has been begun to determine the effect on fatigue of different stress regimes, including uniaxial tension, plane strain bending and torsion fatigue of rectangular cross-section specimens. The work makes use of the associated program on microcrack measurements. The initial studies appear to be extremely encouraging.

(1) Acoustoelasticity

Professional Associates: G. Herrmann, S. Bennett, G. S. Kino,
C. R. Steele

Graduate Students: N. Shaikh, F. E. Stanke.

Two problems associated with measuring shear waves have been given the main attention: (1) the effects of material inhomogeneity and anisotropy; and (2) the design of a satisfactory transducer.

Our main effort during the past three years on stress measurements has been on the development of equipment and techniques for shear wave scanning. Shear waves are necessary for the direct determination of each of the principal stress components and the principal stress directions at each point, from which, for example, the J and M integrals of fracture mechanics can be computed.

The mechanical equipment and control system for shear wave scanning has been constructed and is in good working order. As before, the transducer can be displaced in the horizontal and vertical directions. In addition, a third stepping motor controls rotation of the transducer to obtain the desired polarization. A pneumatic device brings the transducer into contact rapidly but gently, and then retracts the transducer before a change in polarization or horizontal and vertical displacement. The difficulties of alignment have been eliminated so that measurements can be made at a set of points with a high degree of reproducibility (less than 1% change in $\Delta f/f$) when returning to a given point.

In order to obtain satisfactory mechanical coupling between the shear wave transducer and specimen, previous investigators have used inordinate magnitude of pressure, rigid bonding, or viscoelastic gel, none of which are satisfactory for scanning. At Stanford, a transducer with a spherical front face of large radius was developed, which requires a contact force of only 40 N. Subsequently, a transducer with a glass buffer rod was used, with which the wave velocity in the specimen can be obtained from the first front face and first back face echoes. However, much signal strength is lost because of the small ratio of contact area

to rod cross-sectional area. Finally, a new type of transducer has been developed which, so far, seems to be best of all. This consists of the disc of PZT with a rubber disc for a backing. With light pressure, the full face of the PZT must conform to small irregularities of the specimen surface. Signals are very good, calibration tests on aluminum are better than before, and good results have been obtained for steel which were not possible with the previous transducers.

The measurements are highly repeatable, and similar measurements on amorphous glass show no such variations. Thus, the conclusion is that variations of $\pm 20\%$ with a small transducer and $\pm 10\%$ with the larger contact area rubber-backed transducer, found in rolled aluminum, is really due to variations of material texture. Although this feature is a nuisance to the measurement of stress, it possibly contains useful information about the material. The rolling induced orthotropy is of the same order of magnitude as that induced by stress. A perturbation theory for handling this in the general situation when the rolling direction does not coincide with a principal direction of stress has been worked out.

(2) Residual Stress Measurements

Professional Associate: D. M. Barnett

Graduate Student: M. Scott

During the past year, we have focused our attention on the following areas of research:

(1) Separating out the effects of material microstructure (texture) and residual stress on relative acoustic wave velocity shifts in commercial grade aluminum alloys; and

(2) Augmenting experiments performed with longitudinal waves on stressed aluminum alloys by similar acoustic experiments utilizing shear waves of varying polarizations. The goal of this work is the development of methods of rapid reliable nondestructive evaluation of stressed solids.

To date, we have performed a systematic acoustic study of aluminum plates rolled in one particular direction to induce a texture. Tensile samples stressed in uniaxial tension were cut from the rolled plate with tensile axes at differing angles to the rolling (texture) direction. In this fashion, the longitudinal wave stress acoustic constant B was determined as a function of the angle between the tensile axis and the rolling direction. The variation of B with angle was of the same order as the variation of B within a given sample, so that one may conclude that texture effects are not significant in longitudinal wave experiments. Preliminary experiments with shear waves on the same samples indicate texture and material anisotropy have a significant effect on relative velocity shifts.

Our previous work (M. P. Scott) using longitudinal waves to quantitatively deduce residual stresses in axi-symmetric extruded aluminum billets was extremely successful, and we elected to pursue the use of both longitudinal and shear wave scanning to sort out more complex residual stress states. The acoustic experiments require the use of samples which are large enough to yield results at a significant number of scanning points. The easiest complex residual stress state to induce is that in a rolled sample. Rolling facilities at Stanford are not capable of yielding large enough samples; hence, we are in the process of producing samples of the requisite size at Lockheed. Measurements will be made on samples rolled under conditions just less severe than those required to produce failure during rolling by either edge or internal cracking.

(3) Surface Acoustic Wave Study of Fatigue Microcrack Propagation

Professional Associate: D. V. Nelson

Graduate Student: J. S. Chung

A large portion of the total fatigue life of structural alloys is spent in the growth of microcracks, which generally form very early in life, especially in components with stress concentrations (notches). Experimental data on the growth behavior of microcracks is currently

sparse, but interest in this field is increasing rapidly. Virtually all of the data which do exist have been limited to visual measurement of surface length. Knowledge of both length and depth seems necessary for the proper understanding of growth behavior and for the development of analytical methods for predicting growth rate. Based on previous successes in glass and ceramics, the use of surface acoustic wave technology appears promising as a means for early detection of microcrack formation, for monitoring length and depth during fatigue cycling, and for determining crack opening stress.

Since our initial involvement in this program several months ago, we have completed a literature review on fatigue microcrack propagation and cooperated with M. Resch and J. Shyne in exploring the surface acoustic wave technique for flaw sizing in bend specimens of 7075-T651 aluminum. The technique appears viable. We have also designed uniaxial tension, plane strain bending, and rectangular cross-section torsion fatigue specimens. Prototypes of the specimens have been tested and modifications made to achieve designs which are best suited to use of existing transducers, compatible with existing test equipment and which permit applied strains to be computed and measured reliably.

During the remainder of 1980-1981 we will conduct tests in which the surface acoustic wave technique is used to detect and monitor microcracking in the various types of specimens. Both elastic and plastic cyclic straining will be used. (For plastic straining, crack measurements will be made during intermittent cycles of elastic straining). The ability of the technique to detect and monitor cracks growing both under tensile and shear straining will be investigated. These tests are also designed to investigate why the octahedral shear strain criterion for fatigue does reasonably well in correlating life for uniaxial and torsional stress states under elastic straining but fails to do so under plastic straining. We believe the answer lies in the difference in rates of crack growth and in the proportion of life spent in crack growth. Two metals, aluminum 2024-T351 and 4340 steel (condition to be specified) will be tested.

(4) Acoustic Microscope

Professional Associate: C. F. Quate

Graduate Student: Larry Lam

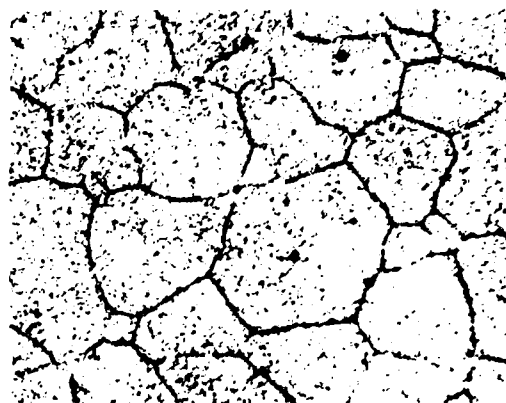
The microprocessor controlled system mentioned in the last annual report has now been coupled to the room temperature instruments. There we have devoted our effort to selected problems in materials. We are finding features in the acoustic micrographs that are destructive and different from those in the optical case.

1. Adhesion of metal films. We have determined that the acoustic reflectance is most sensitive to the adhesion of metal films to the substrate. The lack of adhesion shows up as a change in contrast that is easy to visualize in the micrographs.
2. Oxide films on metals. We have determined that features - such as scratches and cracks in oxide films on aluminum - are clearly recorded with the acoustic microscope. This is again distinct from the optical where details of thin oxides are hard to see. We believe that a study of cracks in these thin films may give us insight into the problem of metal fatigue. The work of Baxter at the GM Research Laboratories indicates that defects in oxide films give the first indication of the onset of metal fatigue.
3. Grains in metals and ferrites. The fact that the acoustic reflection of a focused beam at a liquid-solid interface is sensitive to small changes in the elastic properties permits us to image the grains and grain boundaries in a smooth polished sample. We believe that this will lead to new information on texture and on the nature of the grain boundaries. An example of the grain boundaries in a sample of Inconel, an alloy of nickel, is included in this figure.

INCONEL ALLOY



(a) OPTICAL , POLISHED



(b) OPTICAL , ETCHED



(c) ACOUSTIC $Z = -0.5 \mu$
2.7 GHz



(d) ACOUSTIC $Z = -1.0 \mu$
2.7 GHz

(5) Characterization of Microcracks Using Nondestructive Acoustic Methods

Professional Associates: J. Shyne, D. Nelson, B. Khuri-Yakub,
G. S. Kino.

Graduate Student: M. Resch

The reflection of Rayleigh waves from surface cracks is being used to characterize the geometry of the cracks and their influence on the fracture of materials. The technique is a long wavelength method applicable to small semi-elliptical cracks (smaller than $\sim 500 \mu\text{m}$). Initial efforts were focused on surface cracks in Pyrex glass. That work, now completed, successfully demonstrated the feasibility of the method.

During the last year, the acoustic technique has been adapted so that reflected Rayleigh waves can be used to measure the depth of small (50-100 μm deep) fatigue cracks grown in 7075-T6 aluminum. The acoustic measurements have been made in situ during fatigue tests with the aluminum flexed-plate fatigue specimens mounted in a fatigue test fixture.

The basis of the experimental method is the theoretical relationship between S_{11} , the reflection coefficient of a Rayleigh wave incident on the surface crack, and Δu_z , the acoustic stress-induced crack surface displacement.

$$S_{11} = \frac{j\omega}{4P} \int_A \sigma_{zz} \Delta u_z dA$$

where σ_{zz} is the acoustic stress, P is the power of the acoustic signal, and A is the area of the crack. Substitution of various material and instrumentation parameters and the crack dimensions yields expressions that permit evaluation of the crack depth from the measured acoustic reflection coefficient.

The depth of several shallow ($\sim 100 \mu\text{m}$) surface fatigue cracks from 200 to 600 μm at the surface has been calculated from acoustic data. The calculated crack depths agree well with crack depths inferred from

measured crack opening displacements caused by applying a large static stress.

These experiments suggest that the Rayleigh wave reflection method could provide a versatile new tool for studying the earlier stages of the fatigue process.

(6) Electromagnetic Flaw Detection in Insulating and Poorly Conducting Materials

Professional Associate: B. A. Auld

Graduate Student: M. Riazat

Last year we demonstrated experimentally that a capacitive probe operating at approximately 1 MHz frequency had the capability of detecting surface pits between 100 and 300 μm in diameter on the surface of a silicon nitride sample. This result, and others in the current electromagnetic testing program, have led to sufficient additional funding that this project will be transferred out of the Thrust Program at the end of the present research year. During this final year, our efforts have concentrated on probe analysis and design, aiming toward gaining a better understanding of capacitive probes for the purpose of optimizing their design and quantitatively determining their merits relative to the usual inductive probes. A comprehensive paper is now in preparation, covering the work of capacitive probes supported by the Thrust Program and inductive probes supported by EPRI. Much of this paper is based on the concept of spatial frequency filtering, developed under the EPRI program, but directly applicable to capacitive probes. This approach appears to have solved the knotty problem of how to treat the analysis of capacitive probe field shaping in a realistic and practical way. From an operational point of view, probe design entails shaping the probe fields so as to minimize lift-off effects and optimize sensitivity to the type of flaw under examination. Controlling the spatial frequency spectrum of the probe field enables one to control the depth of penetration into the test sample and also affects lift-off phenomena.

(7) Surface Acoustic Wave Measurement Techniques

Professional Associates: G. S. Kino, S. Bennett

We have so far demonstrated that we can measure stress variations over the cross-section of a metal sample. However, the technique is difficult to apply to the measurement of stress variations into the depth of a sample. Consequently, we have been trying to establish new methods for this purpose. One possibility is to use a focused acoustic beam and move the focal position of the beam. This yields information on the stress variations near the focus. Such work is being pursued on a separate EPRI program. Here we have concentrated on using surface acoustic wave techniques to measure near-surface stresses. At the same time, the surface acoustic wave techniques being applied could be used to measure the details of surface flaws or cracks.

The basic idea then is to excite a surface acoustic wave by means of a wedge transducer and detect the amplitude and phase of the surface acoustic wave reaching a receiving transducer at several points on the surface of the metal. With this information in hand, we should be able to use tomographic computer techniques to determine the variation of stress fields over the surface. By varying the frequency, one should also be able to obtain some information on the variation of stress fields with depth in near-surface regions. The technique should also be applicable to determining variations of microstructure or surface hardness and to determining shape and size of flaws. As an extrapolation of the basic idea, there is also the possibility when looking for flaws of exciting with a bulk wave on the other side of the sample and detecting mode-converted surface waves which occur at cracks.

The initial technique which we set up made use of our mechanically-scanned shear wave Hertzian contact transducer. This transducer, when correctly designed, has a contact area of the order of $50 \mu\text{m}$. Thus, the contact area can be made less than one wavelength in diameter. We were able to show that we could detect surface acoustic wave amplitude and phase with this contacting transducer and we could then mechanically scan the transducer over the surface of the metal and

determine amplitude and phase at each point. By using this method, we were able to detect phase variations due to thin surface layers of the order of 25 μm thick (paint) laid down on the metal surface. However, we found problems with reproducibility because of the extreme mechanical precision required.

We therefore came to the conclusion that it would be better to arrive at a complete non-contacting method. Consequently, during the year, we developed in cooperation with an AFOSR program a laser probe based on work of Ash, in which a laser beam is scattered from the metal surface. After photodetection, the modulation of the laser beam due to an acoustic wave propagating along a metal surface is detected at its original frequency and both its amplitude and phase can be determined. The technique has been developed so that it is not prone to vibration problems. With it we have been able to make accurate measurements of amplitude and phase of a surface acoustic wave on LiNbO_3 and on silicon nitride ceramics.

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2. THRUST PROGRAM ON POLYMERS

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Agency Support:

NSF	ENG 7822167
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NSF-MRL	through CMR

Technical Objective:

The overall objective of the Polymers Thrust program is to establish a predictive relationship between the molecular/morphological properties of poly(vinylidene fluoride) (PVF₂) and the piezoelectric behavior. Insights gained from fundamental materials research on chemical composition, semicrystalline microstructure, mechanical response and electrical behavior can be used ultimately to permit optimization of the material for specific device applications.

Approach:

Samples of PVF_2 of well-characterized molecular structure (average molecular weight, molecular weight distribution, head-to-head defect content) are thermoformed into uniform, thin films under carefully controlled conditions. The film samples are then electrically polarized by holding at high fields while the sample is subjected to a controlled heating/cooling schedule and the piezoelectric coefficients are measured. Differential scanning calorimetry, infrared spectroscopy and X-ray diffraction analysis of polymer samples are used to characterize the crystalline morphology of the polymer and the morphological changes which take place upon mechanical deformation, high temperature annealing or electrical poling.

Research Report:

(1) Background

Polyvinylidene fluoride has attracted widespread interest in the scientific community because of its unique material properties. Its major attraction is its strong piezoelectric activity, with properties similar to crystalline quartz. In addition, it is pyroelectric, has a large nonlinear optical coefficient and has a high dielectric breakdown strength. These interesting bulk electrical properties are coupled with favorable bulk mechanical characteristics such that it may be easily processed into flexible thin films. Other mechanical properties which make the material appealing for acoustic imaging applications are the very low acoustic wave velocity and impedance. Since this combination of electrical and mechanical properties is not available using current ceramic and crystalline piezoelectric materials, PVF_2 raises exciting technological possibilities for the development of transducer arrays and electromechanical devices.

In general, the molecular weight is the most important aspect of the chemical structure for homopolymers, such as PVF_2 , aside from the chemical character of the repeat unit. In addition, since polymerization proceeds on a random basis, a distribution of molecular weights will result, the nature of which can strongly affect the bulk mechanical

properties. A third structural feature, which is particularly important for PVF_2 , is the statistical "head-to-head" defect in the chain backbone caused by the reversal of orientation of one of the monomer units during polymerization. It is also possible that the regularity of the chain structure may be broken up by the inclusion of repeat units of different chemical structure, yielding a copolymer.

Although each of the chemical structural variables is under study, it is essential to recognize that PVF_2 , in common with other high polymers, has a very strong "memory" function. The final material properties depend, not only on the chemical structure, but also on the manner in which the raw polymer resin is processed to final form. The two major processing variables involve changes in the thermal history and the mechanical history. An additional processing variable which has been less explored is the use of sample irradiation at different dose and dose rates to promote chemical crosslinking.

In order to correlate the molecular structure resulting from a particular combination of chemical and processing variables with the bulk piezoelectricity, the morphology of the PVF_2 must be understood on several levels. The coarsest texture involves the phase composition, i.e., the relative contributions from crystalline and amorphous regions. Since the piezoelectric activity has been clearly linked to the crystalline domains, an increase in the bulk crystallinity should lead to higher piezoactivity. An intriguing, and crucial, property of PVF_2 is that the material is polymorphic with at least four distinct crystalline phases. These structures, denoted α , β , γ and δ , may be interconverted by various combinations of thermal and mechanical processing steps. The most important feature is that dipole alignment within the unit cell and, hence, the possibility for bulk piezoelectricity varies for the different structures. Whereas α phase material has no net dipole moment in the unit cell, each of the other phases does. The greatest amount of work has been done with β phase material which, when suitably processed, has a high piezoactivity. Relatively little work has been done on the electrical properties of γ and δ phase PVF_2 .

(2) Homopolymer Films

(a) Chemical Structure

In the early stages of the Thrust program a large number of commercial PVF₂ samples were selected for characterization. The major chemical variables of interest were the molecular weight, as determined from the intrinsic viscosity, and the content of statistical head-to-head defects, as determined by ¹⁹F nuclear magnetic resonance. The major device parameter evaluated in the survey was the insertion loss, which is related through a number of material constants to the piezo-electric activity.

Although the survey is not yet complete, some general comments may be made. First, the viscosity average molecular weights cover the range of about 60,000 to 450,000, with the most common value around 150,000. Second, the head-to-head defect content is quite similar for the classes of samples supplied by a given manufacturer: Polysciences (6.3%), Pennwalt (5.8%) and Solvay (4.5%). Finally, the insertion loss of transducers prepared with film from all but the Solvay and Dynamit-Nobel samples exhibited a variation among the various resins which was of the same magnitude as that for transducers made from the same material. Since the molecular weights and defect contents of the films studied as transducers were comparable, further work is necessary to assess the dependence, if any, of insertion loss on the chemical structure.

In an effort parallel to the survey of commercial PVF₂, the capability for homopolymer synthesis was developed with over 50 trials completed prior to the 1980-81 year. Characterization of these samples during the present year indicates that they fall in the molecular weight range of 100,000 to 250,000, which is similar to commercial materials. More importantly, the defect content for samples polymerized at room temperature can be as low as 3.2% depending upon the remaining synthesis conditions. This low defect content is particularly significant because a study of films prepared by the same procedure for various commercial and Stanford PVF₂ samples indicated that for a molecular weight of about 200,000 the crystallinity increases from 41% to 51% as the defect content drops from 6.1 to 3.4%

(b) Annealing Behavior

Two studies have been performed to assess the effect of high temperature annealing on the morphology and piezoelectric activity. In the first study, α phase PVF_2 was prepared by melting at 500K followed by crystallization at temperatures of 430, 433, 435 and 437K for periods of five hours. Differential scanning calorimetry (DSC) was then used to generate fusion endotherms. From Hoffman-Weeks plots it was determined that the equilibrium melting point and excess free energy of the crystalline domains decrease as the content of head-to-head defects increases. In addition, the critical lamellar thickness increases with increasing defect content and with increasing crystallization temperature. All of these results indicate that a decrease in the defect content leads to greater perfection in the crystalline domains. It remains to be seen whether this higher regularity will lead to greater piezo activity.

In addition, inspection of the thermograms indicated the growth of a new, high melting-phase, which increased in magnitude as the annealing time and crystallization temperature increased. Recent work by Stein indicates that this new phase is the γ polymorph. If this is verified by future work, it may be possible to generate piezoelectrically active bulk material solely by thermal processing, with no mechanical deformation required.

In the second study, the effect of annealing on β phase PVF_2 was examined. Films are usually annealed after stretching in order to heal any mechanical damage incurred during the stretching step. There are indications, however, that this annealing leads to decreased piezoelectric performance. To elucidate the mechanism, three film strips were cut parallel to the stretch direction in a larger film. One strip was kept as a control and the other two were annealed at 393K for fourteen hours, either at constant length or under constant tension. Sections of each of the strips were then poled simultaneously and the resultant transducers were evaluated for piezoelectric activity. In addition, unit cell parameters were determined using X-ray diffraction.

The piezoelectric activity d_{33} was found to decrease with annealing, the decrease initially larger for the film held at constant tension. The most interesting observation is that the decrease in d_{33} correlates directly with the decrease in the a and b unit cell dimensions. A molecular model for this effect has been proposed which considers the van der Waals interaction between fluorine atoms on the chain stems within the unit cell during poling. A reduction in the a - b diagonal distance of only 0.4 \AA can lead to a 70% increase in the van der Waals repulsive energy.

(c) Mechanical Deformation

Fabrication of piezoelectric films from bulk resin is a four-step process: 1) melt pressing of the resin into an α phase film, 2) uniaxial stretching to convert to the piezoactive β phase, 3) annealing to heal any damage from stretching and 4) electrical contact or corona poling to align the dipoles. A facility has been developed at Stanford to accomplish all of the processing steps. Whereas the melt pressing apparatus is standard, the custom built uniaxial stretching device is distinguished by the wide range of elongation rates, from 0.5 to 2000 mm/min at temperatures between 20 and 200°C . A second notable feature is the test procedure used for evaluating d_{33} for the poled films. The poled film is squeezed between two brass anvils at a known pressure. The voltage developed across a capacitor is measured with an electrometer and the charge displaced in the film is calculated. Knowing both the charge and the force applied, the response of the film (d_{33}) in pC/NT (picocoulombs/newton) can be calculated.

A major effort has been devoted to the study of the relationship between uniaxial stretching conditions and piezoelectric activity as a function of temperature. Preliminary experiments at low extension rates had indicated an increase in d_{33} with stretch rate. A new stretching apparatus with greater flexibility was constructed. Using this apparatus, films were stretched at temperatures of 60, 80 and 100°C at stretching rates between 100 and 2000 mm/min. All of the films were shown by X-ray diffraction to be converted entirely to β phase. Those

stretched at 60°C showed the greatest increase of activity with stretch rate ($0.0065 \text{ (pC/Nt)(mm/min)}^{-1}$). Unfortunately, the stretch rate was limited to 950 mm/min by film breakage. The ultimate piezoactivity was 16.9 pC/Nt. The films stretched at 80°C exhibited a lower change of activity with rate ($0.0026 \text{ (pC/Nt) (mm/min)}^{-1}$) but could be stretched at rates of up to 1950 mm/min. These films had an ultimate piezoelectric activity of 18.75 pC/Nt. The films stretched at 100°C showed only small changes in d_{33} with stretch rate. Although a 50% improvement in d_{33} over the 12.5 pC/Nt activity observed for commercially processed film has been achieved, the process is still not yet fully optimized.

Although the major emphasis has been on the uniaxial deformation, melt processing has received some attention. Preliminary studies on a number of different commercial samples indicate that under the standard pressing conditions the apparent crystallinity of the resulting films decreases from 46 to 40% as the molecular weight increases from 60,000 to 170,000. In addition, if the applied force is varied at any one molecular weight, a sharp increase in the density of the film is observed at a particular value of applied force. This density increase, which may be related to changes in crystallinity, is diminished for molecular weights greater or less than 120,000. If these recent results are corroborated by further work, they show considerable promise for providing a new method for preparation of films with enhanced crystallinity.

A number of techniques for characterization of sample morphology have been described. Whereas DSC is best suited to the study of unoriented, well annealed samples, other methods such as density measurements, X-ray diffraction and infrared spectroscopy are more applicable to study the combined effects of thermal and mechanical processing. An additional method in the latter category is the study of permeability. In the last year two systems have been designed and constructed for the measurement of equilibrium sorption isotherms and unsteady state diffusion. From the first apparatus the solubility of a penetrant gas in the polymer may be determined; from the second, the diffusion constant may be obtained. The most significant parameter is the product of the two--the permeability. Measurements of this parameter

with gases of different molecular sizes should provide information on the degree of crystallinity, the size of the crystallites and the tortuosity or interconnectedness of the amorphous matrix. This information should be quite useful in characterizing the changes in sample texture resulting from the processing operations.

d) Irradiation Effects

It has been demonstrated in other polymeric systems that irradiation with ionizing radiation causes changes in the crystalline/amorphous ratio. To test this effect on PVF_2 , samples were γ -irradiated in both the solid and molten states to total doses of 0.1, 1.0 and 10.0 Mrad. Samples made from the irradiated polymer were studied by differential thermal analysis (DTA), X-ray diffraction, infrared spectroscopy and density measurements. The higher dose samples (1.0 and 10.0) showed evidence of the formation of some β phase material. The degree of crystallinity was not significantly altered--the change as calculated from density measurements was less than 5%. There was a change in melting point of 15°C between the lowest and highest melting samples as determined by DTA.

e) Interaction With Device Development Efforts

The Polymer Thrust has a close interaction with the device group in Ginzton Labs. This group has produced a phased acoustic array using PVF_2 and photolithographic techniques. Some of the films used in the development of these arrays were produced in the polymer facilities. Another area of interest in the device group is phase modulation of light traveling through an optical fiber. A PVF_2 clad fiber is required for this application. Preliminary studies have shown that it is possible to imbed optical fibers in PVF_2 .

(3) Homopolymer Fibers

Although the production of piezoelectric films of PVF_2 has led to the possibility of a number of important device applications, it would be an advantage to produce piezoactive material in geometries other than thin films. This need has motivated a study of the possibility of producing piezoactive PVF_2 fibers. Such fibers could then be incorporated into composite materials with a wide range of geometrical shapes. The initial stage of this research is directed towards acquiring a fundamental knowledge of the process of fiber production through flow induced crystallization of macromolecules in solution and melts. Among the methods of producing crystalline fibers, flow operations offer an efficient method which, in principle, could be developed into a continuous process.

The criteria which must be satisfied by the flow field in order to cause crystallinity are that it be both of sufficient strength and sufficient duration to significantly deform and orient the polymer molecules. In order to meet both criteria, extensional flow containing a stagnation point will be studied. An experimental apparatus is currently under construction which will combine light scattering, tensile stress and infrared absorption in order to determine directly the state of macromolecular conformation and the degree of crystallinity in the flow field. Total intensity light scattering measurements will be used to determine the deformed mean radius of gyration of the macromolecules. These measurements will be complemented by homodyne dynamic light scattering measurements which will allow the kinematics of the flow field to be determined.

As a flexible macromolecule is deformed from its random coil configuration, its hydrodynamic friction factor will increase in proportion to its mean size which in turn leads to a dramatic increase in the tensile stress contribution of the polymer in extensional flow. Indeed, the extensional viscosity of a dilute polymer solution can increase by a factor which scales as the molecular weight to the power of three. The tensile stress is, therefore, a sensitive measure of the polymer

configuration and the experimental design will accommodate such a measurement capability.

It is projected that the apparatus will be completed by the end of the summer of 1981. The objectives of the initial experiments will be to determine the flow field conditions which are necessary in order to significantly distort and align macromolecules of various molecular weights. Upon establishing the criteria for the achievement of strong flows, the degree and morphology of crystallinity will be determined as a function of kinematic conditions in the flow and in relation to the molecular conformation.

4) Copolymers

To date, the majority of the research effort has been directed toward determining the appropriate thermal and mechanical processing protocol to apply to a polymer resin with particular chemical characteristics in order to obtain the high piezoactivity β phase. An alternative approach is to incorporate dissimilar repeat units in the chain backbone which predispose the polymer to crystallize in the β form. The very fact that so many different polymorphic states exist indicates that the lattice energies of the different states are not too dissimilar. Thus, a reasonably small chemical change could lead to a significant morphological change.

In order to have the capability of copolymerization, a second generation synthesis rig was constructed during the last year. In addition to the provision for multiple monomer gas admission to the manifold, it includes the capability for multiple cryogenic distillation of the monomer prior to admission to the reaction vessel. This should aid in reducing any impurities in the monomer gas, a factor that can lead to low molecular weights.

5) Blends

The PVF₂ synthesized within the Thrust program is characterized by lower head-to-head defects and higher crystallinity. For reasons that are not yet clear, this material is not well behaved under mechanical processing in that it cannot be stretched easily. In order to understand this phenomenon, the mechanical properties of blends of PVF₂ with silica (SiO₂) and blends of differing molecular weight PVF₂'s were examined.

The addition of SiO₂ to low molecular weight commercial PVF₂, which behaves mechanically similarly to the synthesized material, further degraded the mechanical properties. The blending of high and low molecular weight PVF₂ did improve the mechanical properties. However, large amounts of high molecular weight material may be required to achieve the desired results. The piezoelectric properties of these blended films have not yet been determined.

2-a. PHOTOPHYSICS OF AMORPHOUS SOLID STATE POLYMER BLENDS:
COMPATIBILITY AND RELAXATION BEHAVIOR

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Agency Support:

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NSF-MRL through CMR

Technical Objective:

The objective of this research is to provide a molecular basis for the analysis of the thermodynamics of polymer-polymer interactions and molecular mobility in amorphous solid state polymer blends. Of particular interest is the effect of sample thermal and mechanical processing history on chain conformational rearrangement associated with the glass transition and the sub-glass beta relaxation.

Approach:

The experimental program encompasses the thermodynamics of both compatible and incompatible blends and the kinetics of transformation from one state to the other. For any given blend, the first stage of investigation is the consideration of the degree of dispersion of the guest aromatic vinyl polymer in the host polymer matrix. For thermodynamically compatible blends, of concentration in excess of about 10%, dissimilar polymer chains will be intimately entangled and the local concentration of aromatic rings will be essentially random. In immiscible blends, on the other hand, unfavorable thermodynamic interactions between guest and host polymers will lead to clustering of like species with an increase in the local density of aromatic rings.

The approach taken is to employ excimer fluorescence as a molecular probe of the intermolecular aggregation associated with phase separation (1). The observed ratio of excimer to monomer emission intensities, I_D/I_M , depends both upon the concentration of excimer forming sites (EFS) and upon the efficiency with which the EFS are sampled by the energy migration process.

Once the molecular morphology has been established for a sample with a given processing history, molecular rearrangement associated with sub⁻¹ glass and glass transition phenomena may be studied by heating the solid sample. The application of the excimer probe to detection of segmental mobility is identical in concept to the investigation of rotational diffusion in dilute solution described elsewhere, albeit with considerably different time scales. If the blend is compatible, information on intramolecular segmental motion may be inferred from the observed changes in excimer fluorescence during heating. If the blend is incompatible or undergoes phase separation, information on the increase in local aggregation or chain clustering may be obtained.

Research Report:

In a study of blends of poly(2-vinyl naphthalene) (P2VN) with monodisperse polystyrene (PS) (2) the excimer/monomer fluorescence ratio of the guest P2VN was found to increase rapidly as the molecular weight of the host PS was increased. This change, which occurred before any signs of bulk phase separation were visible, was interpreted as signaling immiscible behavior on a small distance scale. Cloud-point molecular weights and concentrations experimentally measured using excimer fluorescence were predicted with moderate success by Flory-Huggins lattice theory when an empirically determined value of the interaction parameter of 0.010 was used. This experimental value agreed with that predicted by a solubility parameter approach. The excimer fluorescence predictions of miscibility for low molecular weight host matrices were confirmed by differential scanning calorimetry (3).

In addition, blends of P2VN with poly(n-butyl methacrylate) (PnBMA) or poly(methyl methacrylate) (PMMA) were examined using both optical

clarity and excimer fluorescence (4). When blends were prepared by solvent casting at temperatures greater than the glass transition temperature of the binary polymer 1/polymer 2 system, followed by quenching to an examination temperature below T_g , the fluorescence and optical properties were characteristic of the morphology in thermodynamic equilibrium at the casting temperature. The phase relationships for such equilibrium P2VN/PnBMA blends were described quite well by a Flory-Huggins treatment with a temperature dependent binary interaction parameter. All P2VN/PMMA blends prepared by solvent casting below T_g were in nonequilibrium states with apparent miscibilities much higher than predicted by the Flory-Huggins treatment.

Finally, miscible blends of monodisperse polystyrene with poly(vinyl methylether) (PVME) have been studied over the temperature range in which the system is rubbery (5). Under such conditions, the population of excimer forming sites is in thermal equilibrium and may be predicted by rotational isomeric state theory. These calculations were used to determine the temperature range over which exciton migration could be treated as a one-dimensional random walk along the polymer chain.

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3. S.N. Semerak and C.W. Frank, "Excimer Fluorescence as a Molecular Probe of Blend Miscibility: V. Comparison with Differential Scanning Calorimetry," submitted to *ACS Advances in Chemistry Series*, on Instrumental and Physical Characterization of Macromolecules
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2-b. MICRORHEOLOGY OF POLYMERIC LIQUIDS BY TWO-COLOR BIREFRINGENCE

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Agency Support:

NSF-CPE-8025833

NSF-MRL through CMR

Technical Objective:

The objective of this research is to measure the dynamic response of complex polymeric liquids subjected to flow. The work will emphasize fast, nonlinear flow response to transient flows.

Approach:

A modified flow birefringence experiment will be developed on a two-colored laser system which will allow conformational information to be determined at faster rates than previously possible.

Research Report:

The construction of a novel design of a flow birefringence experiment called a "two-color flow birefringence system" has been initiated. The development of this apparatus will allow much faster transient responses of complex liquids to hydrodynamic fields to be measured. Both the flow-induced birefringence and orientation of the flowing material can be simultaneously determined using this concept. The initial studies will focus on rigid rod suspensions used in liquid-crystalline displays subjected to the inception and cessation of simple shear flows.

3. THRUST PROGRAM ON NOVEL CATALYTIC MATERIALS

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Early work by Levy and Boudart showed that carbides of tungsten possess catalytic properties analogous to platinum. From this basic observation it was postulated that compounds of group VIB metals with nonmetals, particularly of groups IVA and VA, may show chemical and catalytic properties similar to rarer, less abundant transition metals such as Ru, Pd, Pt and Ag. Initial studies in this direction were encouraging, as McCarty and Madix showed that surface carbides of nickel decomposed formic acid in a manner similar to copper but different from nickel itself. It was also observed by both the Boudart and Madix groups that the chemical state of the topmost carbon layer on tungsten and nickel respectively, strongly affected the catalytic behavior.

Studies by the Boudart and Madix groups on single crystal overlayers of carbon on W(100) revealed that the structure of the surface carbide, W(100)(5x1)C, consisted of interstitial carbon atoms sandwiched between a hexagonal surface arrangement of W atoms and the square lattice of the bulk planes. Further studies in the Madix group indicated that a single layer of carbon passivated the tungsten (or molybdenum) surface, so that molecules which completely dissociated (CO, CH₃OH, etc.) on clean tungsten to adatoms produced stable molecular fragments (CO, CH₃O, etc.) on the carbide surface. These observations served as a

springboard for theoretical calculations of the electronic structure of the surface by Harrison which indicated that in the formation of the surface carbide tungsten d-levels and carbon 2p orbitals interacted to split off a d state perpendicular to the surface, very near the Fermi level--effectively a dangling bond. The d-states approximately in the plane of the surface were tied up in bonding with carbon and thereby effectively passivated for further chemical affinity with adsorbed species. These theoretical predictions of Harrison were qualitatively substantiated by Stefan and Spicer who showed that on W(100)(5x1)C a sharply defined state existed just below the Fermi level.

As the developments in the electronic state of the surface occurred, the Boudart group was able to synthesize a high surface area Mo_2C catalyst utilizing a temperature programmed carburization of MoO_3 in a flowing CH_4/H_2 mixture. This method affords close control of the carburizing potential of the reacting gas and reduced graphitization and sintering. The site density of this material for CO chemisorption was $4 \times 10^{14} \text{ cm}^{-2}$. This test for site density was an outgrowth of studies done in the Madix group on CO adsorption on the carbided surfaces. The catalytic material exhibited activity comparable to palladium and ruthenium for the hydrogenolysis of butane and the Fisher-Tropsch reaction, respectively. This success prompted further synthesis of high surface area materials described below.

The synthesis and understanding of novel catalytic materials depends critically on surface chemistry and physics, and during the past year we have continued our study of these novel catalytic materials. Knowledge of the electronic structure of the surface is provided by the combined experimental and theoretical work of Professors Spicer and Harrison; the surface chemistry on well-defined surfaces is studied by the Madix group; the Boudart group pursues the synthesis and catalytic behavior of the high surface area materials.

Several significant advances were made during the last year. On the theoretical side we have refined the elementary description of the electronic structure of tungsten carbide which we developed the previous

year. This description was a minimal-basis, nearest-neighbor tight binding theory using parameters developed at that time for transition metals compounds in general. Additional important input became available this year. The first was a first-principles band calculation for bulk WC by Dr. Frank Herman at IBM done in collaboration with Prof. Spicer and P. Stefan. This calculation yielded energies at isolated symmetry points but did not give the symmetry of the states. However, in conjunction with the more complete, but less accurate, tight binding theory calculations by Prof. Harrison it was not difficult to identify the bands, determine the symmetry of the states, and correct the inaccuracies of the simple theory. The combined theoretical approach thus yields energies and symmetries for general points in the band.

A portion of the process of relating theory and experiment has now been completed, by comparing the results of the bulk band structure of WC calculated with a non-self-consistent version of the linearized combination of muffin tin orbitals approach of Dr. Herman with the photoemission results of P. Stefan and Prof. Spicer.

The normal-emission experiments appear to yield roughly a one-dimensional density-of-states for the Γ -A direction. Four experimental structures were correlated in energy with high density-of-states positions near the Γ -A line. Two additional structure appear to be emission scattered into the surface normal from elsewhere in the Brillouin zone, as they could not be located in Γ -A and experimentally displayed no distinct polarization dependence, unlike the previously-mentioned structures. The sharp structure near E_f , directed along the surface normal, previously reported, appears to be a bulk band which just becomes occupied near the A point. Its striking directivity may be a consequence of symmetry-selection rules for the experimental geometry and not evidence of true localization in \vec{k} space. Finally, a puzzling constant-kinetic energy structure seen about 12 eV above E_f has been identified as an Auger transition between the C2s band and the top of the valence band.

Studies were also completed by the Madix group on the poisoning effects of sulfur and oxygen impurities on the W(100)(5x1)C surface. It had been noted earlier in the program that O_2 and H_2S could easily be dissociated on the surface carbide to produce adatoms of oxygen and sulfur. Reactions of methanol and formaldehyde were studied on four surfaces for comparison to W(100) and W(100)(5x1)C which were studied in previous work of this group. The reaction of methanol on W(100)(5x1)C is known to proceed via a methoxy intermediate to produce a number of products including CO, H_2 , H_2CO and CH_4 . The overall reactivity on W(100)(5x1)C is less than on W(100), since the dissociation to C, O and H is suppressed by carbide formation. On the surface oxide (W(100)p(4x1)O), surface sulfide (W(100)p(2x1)S), and on the carbide saturated with oxygen and sulfur, respectively, (W(100)(5x1)C/O and W(100)(5x1)C/S) no significant reactivity was observed. It is clear therefore that both oxygen and sulfur act as poisons for this carbide material.

In addition, new structural features were discovered in the reactivity of several small molecules on carbided molybdenum surfaces. On Mo(100) two carbide structures form at carbon coverages of 0.5 and 0.67 monolayers. Both structures fill adjacent nearest neighbor four-fold hollow sites but leave vacant rows of next nearest neighbor sites along the (11) direction. Whereas CO dissociation proceeds readily on either surface, the dissociative adsorption of N_2 , H_2 and C_2H_4 is sharply reduced; nitrogen adsorption is completely blocked, and the sticking probability of H_2 and C_2H_4 is reduced by one to two orders of magnitude. Furthermore, the associative recombination of C and O atoms on these surfaces differs appreciably from the clean surface. Clearly, the C/O spatial distribution on the surface effects the recombination kinetics. Carbon and oxygen atoms react more readily when the surface is carbon rich. Evidently, ligand effects exerted by oxygen atoms on neighboring carbon atoms stabilize surface carbon, or, conversely, neighboring carbon atoms destabilize carbon.

Perhaps the most significant discovery of the year was the result

of work in the Boudart group which gave us confidence in the relevance of studying surface compounds as model materials for bulk catalysts. In the work of Oyama and Boudart the change in activity of three different molybdenum-based catalysts was studied during the initial stages of the ammonia synthesis from N_2 and H_2 . The three catalytic materials were Mo_2C , MoO_xC_y (designating an oxycarbide of significant oxygen and carbon content), and Mo powder. As the reaction proceeded, the uptake of nitrogen was monitored. For each catalyst the catalytic activity reached its steady-state value when the nitrogen uptake was approximately equal to one monolayer, even though the total nitrogen uptake continued well beyond that point (for Mo powder eventual conversion to the nitride occurs). The important conclusion is that the important factor in determining catalytic behavior is the nature of the material at the surface.

In addition to these results new preparation techniques developed by the Boudart group have led to a high surface area Mo_2N catalytic material. Preparation is accomplished by first reducing MoO_3 to MoO_2 in NH_3 at 720K, followed by temperature programmed nitridation in NH_3 between 720 and 920K. This development is very significant and points to future synthesis of other high surface area metal compounds. This material shows unusual X-ray diffraction features that indicate a preponderance of (100) planes. The crystal morphology is yet undetermined.

4. THRUST PROGRAM ON METASTABLE MATERIALS

H. C. Andersen (Coordinator), Professor, Chemistry
M. R. Beasley, Professor, Applied Physics
A. I. Bienenstock, Professor, Materials Science & Engineering,
Applied Physics
T. H. Geballe, Professor, Applied Physics, Materials Science
& Engineering
A. F. Marshall, Center for Materials Research
R. Sinclair, Associate Professor, Materials Science & Engineering
D. A. Stevenson, Professor, Materials Science & Engineering
G. A. Waychunas, Center for Materials Research

Professional Associates:

T. W. Barbee, Jr.	R. H. Hammond
D. Bouchet	S. J. Poon
J. R. Fox	S. C. Rowland
P. H. Fuoss	W. Warburton

Graduate Students:

W. L. Carter	J. Kwo
S. Celaschi	S. Laderman
S. R. Early	Y. S. Lee
R. D. Feldman	W. P. Lowe
A. Fischer-Colbrie**	D. J. Mael
M. H. Grabow	M. A. Perez
F. Hellman	D. G. Stearns
K. E. Kihlstrom	G. B. Stephenson
D. B. Kimhi*	J. J. Talvacchio
J. Kortwright	R. G. Walmsley

*Received PhD during report period.

**Received MS during report period.

Agency Support: NSF-MRL through CMR

Associated

Programs: AF F49620-78-C-0009
NSF-DMR 73-07692
NSF-DMR 79-08554
NSF-CHE-7809317

Technical Objectives:

The purpose of this Thrust Program is to develop a microscopic understanding of the structure and properties of several types of metastable materials.

Approach:

A coordinated program of preparing amorphous and layered alloys, characterizing them by structural studies, measuring their macroscopic properties, and interpreting their properties using modern statistical mechanical theories.

4-a. STATISTICAL MECHANICS OF GLASS FORMATION

H. C. Andersen, Professor, Chemistry

Professional Associate: J. R. Fox

Graduate Student: M. H. Grabow

Agency Support:

NSF-MRL through CMR
NSF CHE-7809317 (an associated program)

Research Report:

We have completed extensive molecular dynamics computer simulations of the rapid cooling of a one-component monatomic fluid at constant pressure. We observed that crystallization was very likely to occur, but samples that did not crystallize were observed to undergo what appears to be a glass transition. The results show that computer simulations are a practical theoretical tool for studying the glass transition, structural relaxation in atomic glasses, and crystallization in supercooled materials. We are now devising realistic interatomic potentials for the copper-zirconium alloys in order to perform molecular dynamics on this system.

Publication receiving substantial support from CMR/NSF-MRL:

J. R. Fox and H. C. Andersen, "Molecular Dynamics Simulation of the Glass Transition," accepted for publication in the Proceedings of the New York Academy of Sciences.

4-b. THRUST PROGRAM ON METASTABLE MATERIALS AND THRUST-RELATED RESEARCH

A. I. Bienenstock, Professor, Materials Science & Engineering and
Applied Physics

Professional Associates:

P. H. Fuoss
S. C. Rowland
W. Warburton

Graduate Students:

A. Fischer-Colbrie
J. Kortright
S. Laderman
D. G. Stearns
G. B. Stephenson

Agency Support:

NSF-MRL through CMR (Thrust Program on Metastable Materials)
NSF-DMR 73-07692 (Stanford Synchrotron Radiation Laboratory),
an associated program.
NSF-DMR 79-08554, an associated program.

Technical Objectives:

The primary purpose of this work is to investigate atomic arrangements in amorphous materials and to relate them to preparative procedures as well as electronic and electrochemical properties associated with the work of others in the Thrust program. At the same time, we are developing new techniques for such structural studies, utilizing synchrotron radiation. We are also utilizing synchrotron radiation for time-resolved fluorescence studies of electron-hole recombination in amorphous semi-conductors.

Approach:

The basic methods used during the past year were X-ray small angle scattering, X-ray diffraction and extended X-ray absorption fine structure (EXAFS) analyses. In addition, time-resolved fluorescence analysis utilizing synchrotron radiation was performed.

Anomalous Scattering Studies of Amorphous Ge-Se Materials^{1,2}

Professional Associates: P. Fuoss
W. Warburton

During the past year, we have continued the differential anomalous

scattering studies which were developed and described last year. In this procedure, one determines experimentally the derivative with respect to photon energy of the X-ray diffracted intensity from a polyatomic amorphous material, holding constant the scattering vector magnitude, $4\pi\sin\theta/\lambda$. The derivative is evaluated at photon energies just below the absorption edge of a specific element (denoted A) in the material, so that it arises from the change with photon energy of the atomic scattering factor of element A due to anomalous scattering. Fourier transform of the derivative yields a radial distribution function in which all the atomic pairs included contain at least one A atom. That is, it yields the average coordination of species A in the material. Synchrotron radiation is used to perform the experiments.

During this report period, more extensive analysis was performed on the scattering data from amorphous GeSe_2 . It was shown that the Ge is four-fold coordinated and Se is two-fold coordinated in this material, as expected. More interesting, though, was the observation that the second neighbor Se-Se distance is about 0.08\AA longer than the Ge-Ge second neighbor distance. Such an observation could not have been made with either normal radial distribution function analyses or EXAFS.

Structural Studies of Amorphous Ge-Mo Materials

Professional Associates: W. Warburton

Graduate Students: J. Kortright

The structural studies on the amorphous Ge-Mo films are part of a coordinated Thrust program effort to understand the physical properties of these materials. During the past year, we have prepared through sputtering a series of thin film samples of these materials for X-ray diffraction, small angle scattering and EXAFS studies. Towards the end of the year, synchrotron radiation beam time was obtained at SSRL. This was used to perform differential anomalous scattering and EXAFS studies of the Ge coordination in these alloys. Small angle X-ray scattering experiments have also been performed at SSRL to determine if the samples are homogeneous. At the present time, the data from all of these studies are being analyzed.

Structural Studies of the Amorphous Cu-As₂Se₃ Systems³

Graduate Students: S. Laderman

Amorphous alloys of Cu with As₂Se₃ have been studied extensively by us previously utilizing both X-ray radial distribution function and EXAFS analysis. These studies showed that the Cu is four-fold coordinated for alloys containing five or more atomic percent Cu. These studies have, in turn, been used in a variety of theoretical analyses related to the electrical properties of amorphous semiconductors to which such metals have been added. It is now the common expectation that such additions will be four-fold coordinated.

During the past year, we have studied samples of these alloys in which the Cu concentration is well below five percent, suspecting from the electrical properties that the bonding might be different in some of these dilute samples from that in the concentrated alloys. This has turned out to be the case. In one of these samples the Cu near neighbor coordination distance is 2.3 Å as compared to the 2.4 Å normally found in these alloys. This distance is consistent with three-fold coordination of the Cu. This three-fold coordination is, in turn, consistent with that found for Ag in low Ag concentration alloys of that metal with amorphous Ge-Se alloys described in the next section of this report. This finding of three-fold coordination indicates that the bonding of metals in amorphous semiconductors shows greater variety than had been anticipated previously. The implications of these bondings for the electrical properties are presently being studied by us and others. At the same time, we are attempting through additional fluorescence EXAFS studies to determine the preparation conditions and composition range in which this three-fold coordination of Cu is found.

Structural Studies of the Glassy Ag-Ge-S and Ag-Ge-Se Alloys⁴

Professional Associate: S. C. Rowland

Graduate Student: A. Fischer-Colbrie

The structures of approximately 20 glassy alloys with compositions close to the form Ag_x(Ge_{.4}X_{.6})_{1-x}, where X is S or Se and x ranges from 0 to 0.35, have been studied by X-ray radial distribution function analysis. These alloys are closely related in composition to

those formed in the Ag-Ge-X photoresist systems. The most important conclusion of this work is that the average Ag coordination number appears to increase continuously with increasing x from 1.0 ± 1.2 for a sample with $x=0.05$ to 4.0 ± 0.3 for a sample with $x=0.35$. Thus, there appears to be a large composition range over which an appreciable number of Ag atoms are coordinated by fewer than 4 atoms. This result is consistent with the previously discussed work of Laderman on the Cu-As-Se system, which also indicated such deviations from the now commonly anticipated fourfold coordination. This work is now being prepared for publication. We are also seeking to verify these conclusions, and relate them to amorphous films formed by photodiffusion, through EXAFS studies.

Dynamic Small Angle X-ray Scattering

Professional Associate: W. K. Warburton

Graduate Student: G. B. Stephenson

The goal of this work is to be able to monitor the development with time of various structural features of amorphous materials like phase separation and void growth utilizing synchrotron radiation to detect time-resolved small angle X-ray scattering.

During the past year, G. B. Stephenson has developed a Reticon linear diode array detector, its support electronics and operating software. The detector was installed in a vacuum housing, special low noise switching circuitry was built and an SSRL CAMAC based 8080 micro-processor programmed to digitize the detector output and subtract off background counts. This detector is a diode array of 1024 elements, each $0.001''$ by $0.100''$ and acquires a complete small angle scattering pattern in each "exposure." It has been optimized for high flux acquisition of patterns which are evolving continuously (and non-cyclically) with characteristic times of 1 second or less.

During the late Spring and next year, it will be utilized to study the above-mentioned types of phenomena in amorphous materials. It will also be used to monitor the precipitation of asphaltenes in heavy crude oils, in collaboration with K. S. Liang and R. Long of the EXXON Research and Engineering Company.

Early Photoluminescence Decay in Amorphous Si:H

Graduate Student: D. Stearns

Because amorphous hydrogenated silicon (a-Si:H) has recently become a promising material for photovoltaic applications, its electronic properties are of considerable interest. In this work electron-hole recombination processes are being studied utilizing time-resolved photoluminescence (PL). It has become apparent, as a result of earlier work, that PL decay in a-Si:H arises from two different types of recombination. For times greater than 10^{-7} seconds after excitation, the electrons are trapped in localized states and recombine by tunneling to neighboring sites. For times less than 10^{-7} sec, the PL decay is approximately exponential and is thought to arise from the geminate recombination of electron-hole pairs. We have measured, for the first time, PL decay in the time regime of 10^{-10} to 10^{-8} sec as a function of temperature, excitation energy and emission energy. Our intention is to analyze the early PL decay in terms of possible models for electron-hole recombination.

In this experiment, we use synchrotron radiation (SR) provided by SSRL as the light source. SR has two very useful properties. The inherent pulse structure of the light (200 psec FWHM and megacycle repetition rate) makes it well-suited for high resolution time-resolved spectroscopy. In addition, the broad-band tunability of the source allows us to study easily the dependence of the PL decay on excitation energy.

We are, at present, in the process of analyzing the data. The early PL decay that we have measured agrees qualitatively with the results of other groups. The early decay rate increases with increasing temperature and emission energy. The PL decay rate decreases with increasing excitation energy. These characteristics are consistent with a model of geminate electron-hole pairs that thermalize together into the band tails and there recombine radiatively.

References:

1. P. H. Fuoss, P. Eisenberger, W. K. Warburton and A. Bienenstock, "Application of Differential Anomalous X-ray Scattering to Structural Studies of Amorphous Materials, " Phys. Rev. Letters 46 1537 (1981).
2. P. H. Fuoss and A. Bienenstock, "X-ray Anomalous Scattering Factors - Measurement and Applications," invited paper to be published in the Proceedings of the International XUV Conference, Stirling, 1980.
3. S. Laderman and A. Bienenstock, "EXAFS Investigation of Dilute Cu Impurities in Amorphous As_2Se_3 ," to be published in the Proceedings of the Ninth International Conference on Amorphous and Liquid Semiconductors, Grenoble, 1981.
4. S. C. Rowland, L. C. Bourne and A. Bienenstock, "Radial Distribution Function Studies of Glassy Germanium-Silver-Chalcogen Alloys," *ibid.*

4-c. SYNTHESIS AND LOW TEMPERATURE PROPERTIES OF NEW MATERIALS

T. H. Geballe, Professor, Applied Physics and Materials Science and
Engineering

Professional Associates:

R. H. Hammond
T. W. Barbee, Jr.
S. J. Poon

Graduate Students:

S. Celaschi	J. Kwo
W. L. Carter	W. P. Lowe
S. R. Early	F. Hellman
R. D. Feldman	D. J. Mael
K. E. Kihlstrom	M. A. Perez
D. B. Kimhi	J. J. Talvacchio

Agency Support:

AF F49620-78-C-0009
NSF-MRL through CMR - Thrust Program on Metastable Materials

Technical Objective:

To prepare new or unusual superconducting and magnetic compounds and composite structures and to study their mechanisms and interactions responsible for their behavior.

Approach:

Techniques such as electron-beam evaporation, sputtering, arc melting, and vapor transport are used to prepare crystals, compounds or materials of interest. Their electronic properties are then correlated with their structural properties by investigating superconducting transitions, heat capacities, optical and transport properties including tunneling.

(1) New and Unusual Composites and Amorphous Phases by Vapor Deposition

Professional Associates: T. W. Barbee, Jr. and S. J. Poon

Graduate Students: W. L. Carter, S. R. Early, D. B. Kimhi,
W. P. Lowe

Enhancement of $H_{c2}(T)$ above the values predicted by the Ginzburg-Landau-Abrikosov-Gorkov (GLAG) theory has been observed consistently in amorphous transition metal alloy superconductors by other groups. We have prepared thin films of amorphous Mo-based two-component alloys by vapor phase codeposition on sapphire substrates which do in fact obey GLAG theory. A phenomenological model has been developed in terms of which all present experimental results can be understood. The model is applicable to materials in which fine-scaled spatial variations occur. Such situations can easily arise in any metastable system; thus the model may have wide applications.

The question of coherent interfaces between multilayers of sputtered Nb and Cu has been addressed using x-ray scattering. It was found that the interfaces were not coherent as had been previously claimed by other workers. The NbCu multilayers are found to be composed of columns strongly layered along the growth direction. The height of the columns is about 5 times the modulation wavelength Λ . The resistivity increases monotonically with Λ^{-1} reaching $72.6 \mu\Omega\text{-cm}$ for $\Lambda = 18.3 \text{ \AA}$. The superconducting transition temperatures are all below 4.2K.

Reference Publications:

1. "Superconductivity and Paramagnetic Impurities in KC_8 ," by F. J. DiSalvo, P. H. Schmidt, G. W. Hull and T. H. Geballe, Am. Phys. Soc. 25, 297 (1980).
2. "An Attempt to Synthesize the Superconducting Phase of CdS Using Shock Compression and Recovery," by B. W. Dodson, R. A. Graham, B. Morosin, J. E. Schirber and T. H. Geballe, Bull. Am. Phys. Soc. 26, 413 (1981).
3. "Enhanced Critical Field Curves of Metastable Superconductors," by W. L. Carter, S. J. Poon, G. W. Hull, Jr. and T. H. Geballe, to be published in Solid State Communications.

4. "A Silicon on Sapphire Thermometer for Small Sample Low Temperature Calorimetry," by S. R. Early, F. Hellman, J. Marshall and T. H. Geballe, to be presented at the LT16 Conference, University of California, Los Angeles, August 19-25, 1981.
5. "X-ray Scattering from Multilayers of NbCu," by W. P. Lowe, T. W. Barbee, Jr., T. H. Geballe and D. B. McWhan, submitted to Phys. Rev.

(2) Synthesis and Properties of Superconducting Compounds

Professional Associates: R. H. Hammond and B. Pannetier

Graduate Students: K. E. Kihlstrom, R. D. Feldman, J. Kwo, F. Hellman, J. Talvacchio, S. Celaschi, M. Perez, D. J. Mael.

Metastable compounds primarily with the A15 phase are being synthesized by codeposition using beam-techniques. The three colinear electron-beam source facility has been improved so that the deposition parameters and the growth process can be controlled more carefully. Efforts are being made to extend the phase boundaries of the high superconducting transition temperatures (T_c 's) of the compounds Nb_3Al , Nb_3Ge , and Nb_3Si toward the metalloid-rich side using epitaxy, and laser annealing. Tunneling into the metastable A15 compounds is being employed. Analysis obtained by deconvoluting the tunneling data shows that films which approach the metastable stoichiometric composition become strongly coupled at least in part by virtue of a pronounced phonon softening. It has been suggested that strain energy contributes an additional term to the free energy, asymmetric with respect to composition which must be explicitly included to account for metastability, phonon softening and observed high T_c 's in Nb_3X series ($X = Al, Ge, Ga,$ and Si). Nb-rich Nb_3Si films with the A15 structure have been epitaxially grown onto prepared substrates in which the Si concentration has been extended towards equilibrium. They have been studied by transmission electron microscopy and an understanding of the role of O_2 in stabilizing the high T_c phases has emerged.

Reference Publications:

1. "Ultrasonic Attenuation of Surface Acoustic Waves in the Thin Film of Superconducting Nb_3Sn ," by H. P. Fredricksen, H. L. Salvo, Jr., M. Levy, R. H. Hammond and T. H. Geballe, Physics Letters 75A, 389 (1980).
2. "Epitaxial Growth of $Al_5 Nb_3 Si$," by R. D. Feldman, R. H. Hammond and T. H. Geballe, IEEE Trans. Mag. MAG-17, 545 (1981).
3. "Superconductivity in Electron-Beam Codeposited $Al_5 Mo-Nb-Si$ Alloys," by S. J. Poon, R. H. Hammond and T. H. Geballe, submitted to Journ. Vac. Sci. Tech.
4. "CW Laser Annealing of $Nb_3 Al$ and $Nb_3 Si$," by T. Shibata, J. F. Gibbons, J. Kwo, R. D. Feldman and T. H. Geballe, to be published in the Journal of Applied Physics.
5. "Superconducting Tunneling into the $Al_5 Nb_3 Al$ Thin Films," by J. Kwo and T. H. Geballe, Phys. Rev. B 23, 3230 (1981).
6. "Superconductors in Electric-Power Technology," by T. H. Geballe and J. K. Hulm, Scientific American 243, 112 (November 1980).
7. "Stabilization and Strong Coupling Properties of High Transition Temperature Superconductors," by T. H. Geballe, R. H. Hammond and J. Kwo, presented at the AIPE Fall Meeting, Pittsburgh, October 1980, and to be published.
8. "Superconducting Tunneling as a Function of Composition into $Al_5 Nb_3 Ge$ Thin Films," by K. E. Kihlstrom, J. Kwo, R. H. Hammond and T. H. Geballe, Bull. Am. Phys. Soc. 26, 211 (1981).
9. "The Dependence of Flux Line Pinning on Composition in $Al_5 Nb-Sn$ Superconductors," by J. Talvacchio, R. H. Hammond and T. H. Geballe, Bull. Am. Phys. Soc. 26, 478 (1981).
10. "CW Laser Annealing of Al_5 Superconductors," by B. Pannetier, T. H. Geballe, R. H. Hammond and J. F. Gibbons, to be presented at the LT16 Conference, University of California, Los Angeles, August 19-25, 1981.

4 d. THRUST PROGRAM ON METASTABLE MATERIALS

A. F. Marshall, Research Associate, Center for Materials Research
R. Sinclair, Associate Professor, Materials Science and Engineering

Professional Associate:

D. Bouchet

Research Report:

Research efforts in the past year have focused on the crystallization behavior of amorphous Cu-Zr alloys. TEM characterization has been used in conjunction with DSC and x-ray diffraction to compare vapor-quenched (VQ) with liquid-quenched (LQ) alloys of the same composition (Cu-40 at% Zr). Amorphous phase separation, also observed at this composition under certain deposition conditions [1], was characterized using STEM techniques [2]. Intermetallics in the Cu-rich end of the phase spread formed by annealing the amorphous material were studied using convergent beam diffraction [3]. This work was done in conjunction with the Stevenson group.

(1) Comparison of LQ and VQ Material

The composition studied was Cu-40 at% Zr. This could be obtained as a single-phase or as a phase-separated amorphous structure according to the mode of sputter-deposition (SD) employed. The crystallization behavior of the single-phase SD material was compared with a study done on LQ material of the same nominal composition as reported in the literature. The glass transition and crystallization temperatures (T_g , T_c), and the changes in temperature and heat of crystallization (T_c , ΔH_c), as a function of annealing below T_g , were observed using differential scanning calorimetry (Stevenson group). The crystallization products, microstructure and compositional changes were studied using x-ray diffraction and analytical TEM techniques (Marshall, Sinclair, and Stevenson groups).

The thermal behavior of the SD material was very similar to that of LQ material with small discrepancies (e.g., slightly different T_g) which could be explained by a difference in composition of a few atomic per cent. Exothermic peaks indicated three crystallization steps which varied as a function of prior annealing treatment in qualitatively the

same way. The partially crystallized structure, as observed in TEM, contained crystallites of the intermetallic $\text{Cu}_{10}\text{Zr}_7$ phase (41.2 at% Zr) surrounded by an amorphous matrix. The crystallites were composed of elongated subgrains, 300-500Å in width. The same type of structure has been observed for partially annealed LQ material. Energy dispersive analysis gave some indication of Cu enrichment of the amorphous matrix adjacent to the crystallites. The crystallization process thus appears to be one of nucleation and growth of the primary phase. It appears that the first two exothermic peaks are related to this primary crystallization process, while the third peak is related to final crystallization of the remaining Cu-rich amorphous matrix.

The similarity in crystallization behavior of VQ and LQ alloys suggests that their amorphous structures are also very similar. This is quite significant for structures prepared by very different physical processes.

(2) Amorphous Phase Separation

Amorphous phase separation was previously observed in Cu-40 at% Zr deposited in a phase spread mode [1]. This was further characterized using improved specimen preparation techniques and STEM analysis, i.e., microdiffraction and energy dispersive spectrometry (EDS) [2]. A wavy microstructure of dark and light areas, 100-300Å in width, was observed. This appearance was a result of mass thickness contrast, as shown by tilting the specimen. The dark areas had a larger average interatomic spacing than the light areas, as shown by the diffuse amorphous ring of the electron microdiffraction patterns. These spacings could be correlated with the split peak of the corresponding x-ray diffraction pattern. EDS showed the dark areas to be a Zr-rich phase, and the light areas a Cu-rich phase.

(3) Convergent Beam Diffraction

Convergent beam diffraction (CBD) was used to study the crystal structure of Cu-Zr intermetallics obtained by annealing the amorphous material. (CBD is a microdiffraction technique giving symmetry information for individual crystallites in a microstructure.) The aim was two-

fold: (1) to characterize intermetallic phases in the fully annealed structures (annealed above T_c to obtain complete crystallization), and (2) to be able to identify phases in partially crystallized structures (annealed below T_c).

Results are presented for two intermetallic phases in fully annealed specimens:[3] (1) $\text{Cu}_{3.6}\text{Zr}$ (21.7 at% Zr): The space group given for $\text{Cu}_{3.6}\text{Zr}$ in the literature is $P6/m$; our studies showed a forbidden reflection along the c-axis and a resulting space group $P6_3/m$. The unit cell was therefore doubled in the c-direction. A crystallographic map of the major zone axis patterns was made, and the existence of this phase in partially annealed specimens could be quickly determined with reference to the map. (2) Cu_9Zr_2 : 18.2 at% Zr. Several stoichiometries from 16-20% Zr were proposed for this phase and no structural data was available. We obtained this phase by annealing at 825°C , but it did not occur when annealing at a lower temperature of 500°C . CBD showed it to have a long period superlattice structure based on an fcc sublattice. The superlattice had tetragonal symmetry and was rotated 45° about the c-axis with respect to the sublattice. The long period ordering was not completely regular, thus allowing the structure to accommodate a range of compositions. This may explain the various stoichiometries given in the literature. The variations in ordering are currently being investigated by high resolution structure imaging.

Reference Publications

1. T. W. Barbee, Jr., R. G. Walmsley, A. F. Marshall, D. G. Keith, and D. A. Stevenson, "Phase Separation in Vapor Quench Synthesized Noncrystalline Copper Zirconium Alloys," *Appl. Phys. Lett.*, **38**, 132 (1981).
2. A. F. Marshall and R. G. Walmsley, "Amorphous Phase Separation in Vapor-Quenched Cu-Zr," accepted for presentation, 39th Ann. Mtg. EMSA, Atlanta, GA, 1981.
3. A. F. Marshall, J. W. Steeds, D. Bouchet, S. L. Shinde, and R. G. Walmsley, "Crystal Structure Analysis of Cu-Zr Alloys by Convergent Beam Diffraction," *ibid.*

4-e. THRUST PROGRAM ON METASTABLE MATERIALS

D. A. Stevenson, Professor, Materials Science & Engineering

Graduate Students: R. G. Walmsley and Y. S. Lee

Electrochemical Characterization of Amorphous Materials

Technical Objective: The objective of this program is the development and use of electrochemical techniques to characterize amorphous films. These characterization techniques are coordinated with synthesis techniques for films, especially using magnetron sputtering, and with parallel microscopy and thermal characterization tools.

Approach: There are presently two electrochemical techniques which are used for characterizing films. One technique, already extensively developed, is the potentiodynamic anodic polarization technique using a small area working electrode. This technique allows the evaluation of the corrosion resistance of films using small areas of samples (4 mm^2). Many of the samples used in this study are prepared by the phase spread technique using magnetron sputtering. With this technique, in conjunction with the small area cell, samples with a large range of compositions can be obtained in a single sputter synthesis. The electrochemical studies are closely coupled with parallel characterization investigations using X-ray diffraction (XRD), transmission electron microscopy (TEM), and differential scanning calorimetry (DSC).

A second electrochemical technique, presently being developed, uses a membrane - double cell arrangement to study hydrogen permeation in films. This technique allows an assessment of hydrogen diffusivity and solubility of the film in question. With both of these studies, the main objective is to correlate the properties in question to the composition, synthesis conditions, and parallel characterization results.

Research Report:

A. The influence of Composition and Preparative History on the Corrosion of Amorphous Cu-Zr Alloys

The differences in corrosion behavior between amorphous and the corresponding crystallized Cu-Zr alloys were studied using a potentiodynamic polarization technique. The alloys studied were in the

composition range 16-80 atomic % Zr in Cu and were prepared mainly by magnetron sputtering. The amorphous state showed superior passive behavior when extensive compositional modulation occurred upon crystallization; however, there were no significant differences when the crystallized state was compositionally homogeneous, as occurs for overall compositions coinciding with the intermediate phases. Amorphous alloys containing compositional inhomogeneities showed inferior corrosion behavior in contrast to homogeneous amorphous alloys. It is concluded that any improvement in corrosion behavior for the amorphous state arises from a homogeneous composition.

B. Thermal Behavior of Cu-Zr Amorphous Alloy Prepared by Magnetron Sputtering

The thermal behavior of a single phase amorphous Cu-40% Zr alloy, synthesized by magnetron sputtering, was investigated. As-quenched and annealed specimens were characterized by X-ray diffraction, differential scanning calorimetry and transmission electron microscopy. The as-quenched alloy manifests a glass transition, $T_g = 440^\circ\text{C}$, and three exotherms. Devitrification originated by primary nucleation and growth of $\text{Cu}_{10}\text{Zr}_7$ from an amorphous matrix; however, morphologies were quite different for crystallization above and below T_g . The thermal behavior of this alloy is similar to that observed of liquid quenched (LQ) alloys of similar composition. The observation of a T_g for a sputtered alloy and a similarity to LQ alloys is noteworthy.

C. Permeation Studies

A double electrochemical cell permeation system was constructed and the technique for its application to diffusion studies was developed. In this cell, hydrogen is electrochemically pumped into one side of the membrane and removed at the other side; the chemical potential of hydrogen is controlled or measured by either controlling or measuring corresponding cell potentials, and the hydrogen input and output is obtained by monitoring the cell current of both cells. Several combinations of potentiostatic or galvanostatic polarization techniques can be used to measure the diffusion coefficient, the most promising being the measurement of breakthrough time or lag time when abrupt polarization changes are imposed on the cell. The present system

was tested using Armco iron and the results obtained are in good agreement with literature values for hydrogen diffusion. It appears that the cell is operating effectively.

Major activity has been devoted to designing and synthesizing suitable samples for this study which comply with the following requirements: high (measurable) permeability of H_2 at room temperatures in the membrane in question; mechanical integrity (membrane must be free standing and free of pores); and absence of surface layers or poisons that modify the surface electrochemical reactions. The latter problem is sometimes solved using a thin coating of Pd at both electrode interfaces. This is a viable solution when one has a relatively thick and strong membrane that is self supporting and which also has a sufficiently high hydrogen permeability. For materials with low diffusivity, however, it is necessary to study very thin films which are too thin to manipulate without destroying their integrity. A possible solution for this problem is the deposition of very thin layers of amorphous metals on thick layers of palladium; the palladium plays the role of substrate, surface passivity layer, and support. The mathematics of transport through this composite membrane is not trivial, however, this approach seems viable for the determination of the diffusivity of hydrogen if the system is suitably analyzed.

Publications

1. T.W. Barbee, Jr. R.G. Walmsley, A.F. Marshall, D.L. Keith, and D. A. Stevenson, "Phase Separation in Vapor Quench Synthesized Noncrystalline Copper Zirconium Alloys", Appl. Phys. Lett. 33(3)1981.
2. R.G. Walmsley and D. Bouchet, "Thermal Behavior of Cu-Zr Amorphous Alloy Prepared by Magnetron Sputtering", Extended Abstract, Electrochemical Society Meeting, October 1981.
3. R.G. Walmsley and D. A. Stevenson, "The Influence of Composition and Preparative History on the Corrosion of Amorphous Cu-Zr Alloys", Extended Abstracts, Electrochemical Society Meeting, October 1981.
4. A.F. Marshall and R.G. Walmsley, "Amorphous Phase Separation in Copper Zirconium", 39th Annual Meeting of EMSA, Atlanta, GA, August 1981.
5. A.F. Marshall, J.W. Steeds, D. Bouchet, S.L. Shinde and R.G. Walmsely, "Crystal Structure Analysis of Copper-Zirconium Alloys by Convergent Beam Diffraction", 39th Annual Meeting of EMSA, Atlanta, GA, Aug. 1981.

4-f. THRUST PROGRAM ON METASTABLE MATERIALS

G. A. Waychunas, Research Associate, Center for Materials Research

Development of facilities:

During the past year considerable progress has been made in the development of a high sophistication laboratory radial distribution function (RDF) analysis system. In contrast to past years where diffuse x-ray scattering data were collected on paper tape, transferred to magnetic tape and then read into the main campus computer system, data are now preprocessed in the x-ray laboratory and transferred directly to the campus system via a direct hard-wired line. Laboratory preprocessing includes background subtraction, noise filtering, scaling, Compton scattering correction and formatting. This work is performed with a graphics CRT terminal and digital plotter to allow direct inspection of manipulated data.

Research Report:

(1) Characterization of Cu-Zr alloys and amorphous phases

Bulk x-ray diffraction methods have been applied to the differentiation of the various crystalline and amorphous phases observed in the Cu-Zr system in vapor deposited samples (Stevenson group). Also, in conjunction with the Sinclair-Marshall and Stevenson groups, analysis of crystallization behavior as a function of annealing temperature were performed. These studies were conducted by graduate student Robert Walmsley, and constitute a major part of his dissertation research.

(2) RDF analysis of Mo-Ge amorphous alloys

A 10 micron thick Mo-Ge amorphous alloy sample of composition $\text{Mo}_{.567}\text{Ge}_{.433}$ was reconfigured to allow efficient reflection diffuse x-ray intensity measurements. Data collected with Ag K radiation were corrected and Fourier transformed from the k-space range $0-21 \text{ \AA}^{-1}$ to the R space range $0-10 \text{ \AA}$. The first major RDF peak is asymmetric, occurring at a distance of 2.70 \AA with a shoulder extending to 3.15 \AA . The area under this peak is consistent with 10-12 near neighbor atoms, and the distances are similar to those observed for Mo-Ge and Mo-Mo bonds in Mo-Ge crystalline phases. Ge-Ge bonds, which have

lengths of about $2.44 - 2.71 \text{ \AA}$ in crystalline Ge and Mo-Ge phases appear to be somewhat disfavored in the amorphous alloy.

Work is continuing on the generation of RDFs for a complete compositional series of Mo-Ge amorphous alloys.

5. THRUST PROGRAM ON METALWORKING AND PLASTICITY

A. K. Miller, Associate Professor, Department of Materials Science and Engineering (Coordinator)
D. M. Barnett, Professor, Materials Science and Engineering
E. H. Lee, Professor, Mechanical Engineering
O. D. Sherby, Professor, Materials Science and Engineering

Professional Associates:

R. L. Mallett
I. Yarita

Graduate Students:

S. M. DeJesus III
M. P. Scott+
T. Tanaka
T. B. Wertheimer
I. Al-Khattat+
K. Chung*

+Received Ph.D. during report period.

*Received MS during report period

I. Introduction and Objectives

During the years through 1978-79, this Thrust program focussed largely on the problem of room-temperature extrusion. The goal was to create and demonstrate an ability to understand and predict metal flow during extrusion, and its effect on subsequent mechanical properties. Specific sub-tasks included hydrostatic extrusion experiments, development of a finite-element analysis to predict extrusion response, and experimental determination of residual stresses in the product as a means of checking the analytical predictions.

During 1978-79, a major new direction was adopted as a goal for this Thrust program, namely warm rolling of steels. While still within the general area of metal working, the warm rolling problem presents several new challenges. The first and major one is that the elevated temperature environment requires that several additional deformation phenomena be considered: strain rate sensitivity, recovery, approach to steady-state flow, grain boundary sliding, grain size refinement, and, in general, the temperature and history dependence of plastic flow.

The need to treat these phenomena has led to the use of the "MATMOD" constitutive equations in this program which has, in turn, required research on the appropriate numerical methods for their utilization. The second new challenge is that fracture is a limiting factor during warm rolling: total or per pass reductions which are excessive can result in "alligatoring," "crocodiling," or edge cracking. Thus a useful analysis of warm rolling requires a prediction of fracture. Hence development of a local fracture criterion in order to predict the "forming limit" during warm rolling has become an objective. The third new challenge is the question of rolling contact boundary conditions. Unlike the extrusion problem, in which relative sliding between the die and the workpiece occurs across their entire common surface, in rolling one unknown portion of the material is in "sticking" contact with the workpiece, another portion slides in one direction, and another portion slides in the opposite direction.

The remainder of the report summarizes progress in these areas.

II. Accomplishments during 1980-81

A. FINITE-ELEMENT ANALYSIS (E. H. LEE AND R. L. MALLET)

The feasibility of carrying out the large deformation elastic-plastic analysis required for study of metal forming processes has been demonstrated in our previous work. The resulting finite-element digital computer code, IFDEPSA (Incremental Finite Deformation Elastic-Plastic Aalyzer), has undergone steady development in order to improve its efficiency and accuracy and to extend its capability to handle various boundary conditions which can arise in metal forming operations.

We have recently completed a comprehensive study to determine the best finite element and stress updating strategy for use in large deformation elastic-plastic problems. The performance of ten different elements was compared by carrying out a complete extrusion analysis with each element and then comparing the resulting steady-state stress fields. The results demonstrated that higher order isoparametric elements do not live up to their initial promise and that, for comparable computational effort, the most accurate stress fields are given by a four-noded isoparametric quadrilateral employing different orders of numerical

integration for its dilatational and deviatoric stiffness.

One major difficulty in analyzing practical metal forming processes is the modeling of metal-tool interfaces for satisfactory finite-element computation, i.e. the specification and implementation of boundary conditions on the deforming metal's surface. One must first face the fact that the boundary conditions for a material point of the deforming metal's surface change abruptly as the point makes contact with the tool and again when separation occurs. The locations of such points are often not known a priori and must be determined as part of the solution. In the rolling process the situation is further complicated in the region of contact by the fact that slipping occurs near the endpoints while a no-slip condition prevails elsewhere. This means that the location of two additional points of transition must be continuously determined. Thus each surface material point encounters four boundary condition discontinuities where, for example, one traction component boundary condition becomes a condition on the corresponding velocity component or vice versa. Tentative procedures have been devised for handling most of these difficulties in a finite-element context and are currently being tested.

For warm forming a time-rate-dependent plasticity law governs the stress-deformation behavior and we are using the MATMOD equations which were developed to apply in such circumstances. These have been generalized somewhat to apply in three-dimensions in the presence of large strains and rotations since these occur in many metal forming operations.

The kinematical relation that the elastic strain rate is the difference between the total strain rate and the plastic strain rate, in combination with Hooke's law, then gives a relation for the stress rate in terms of the total strain rate and stress history. This can be substituted into the principle of virtual velocities for an increment of strain in a process involving finite strain, which can then be utilized in a finite element formulation to provide a solution procedure for the velocity field and hence the increment of displacement which provides the basis for the next step in the solution. We are now looking for efficient and accurate means of carrying out this process.

So far we have restricted our analysis to isothermal deformation, but with warm forming, cooling to the metal-working dies and the atmosphere combined with heating due to the dissipation of mechanical energy in plastic flow can lead to appreciable temperature variations. In the warm forming temperature range, such variations have an appreciable effect on the strain rate distribution, and we are including the appropriate heat conduction equation to couple with the velocity field relations. Although plastic flow is a non-linear irreversible phenomenon, experiment has revealed a simple law for the thermal influence of mechanical energy dissipated by plastic flow.

B. DETERMINATION OF ROLLING CONDITIONS WHICH PRODUCE SOUND MATERIAL OR FAILURES (Dr. Oleg D. Sherby; Simeon de Jesus III)
Results of Rolling of 1020 Steel and Ultra-High Carbon (UHC) Steels

Mild steel (1020 and UHC steels (52100 and 52150) have been rolled at Stanford (2.5 inch diameter rolls) and at Lockheed (8.25 inch diameter rolls). 1020 has been both cold - and warm-rolled; while UHC steels have been mostly warm-rolled. On only one occasion has cold-rolling of 52100 been attempted.

The results of rolling 1020 are as follows: Cold-rolling leads to alligating at effective strains of $\epsilon = 0.9$ to $\epsilon = 1.2$. A reduction of 5% (and slightly higher) per pass is maintained. At higher temperatures (427°C, and 500°C,) and the same amount of reduction per pass, alligating still takes effect though at effective strains of $\epsilon = 0.6$ to $\epsilon = 1.2$. In particular, at 427°C, less effective strains ($\epsilon = 0.6$) at the point of alligating and 'blue brittleness' are observed in rolled 1020 specimens. At 540°C and much higher temperatures, rolling of 1020 results in no visible defects to the material.

Rolling of UHC steels leads to the following results: On the one occasion that 52100 had been cold-rolled, severe edge cracks (leading to breaking of the specimen into several pieces) prevented further rolling at $\epsilon = 0.6$. Warm-rolling (500°C and higher temperatures) at 5% reduction per pass of 52100 though is easily carried out to extremely large effective strains ($\epsilon = 1.5$ and higher) without any detectable failure of the workpiece. Note that 52100 can be rolled effectively at

a lower warm-rolling temperature than 1020-500°C compared to 600°C respectively.

No cold-rolling had been undertaken for 52150. Warm-rolled 52150 shows alligatoring at 540°C at approximately $\epsilon = 0.8$ to $\epsilon = 1.0$ reductions at 5% (and slightly higher) per pass. At 600°C and higher temperatures, it is possible to roll 52150 specimens to very large strains without encountering any rolling defects. Compared to 52100, 52150 responds less favorably to warm-rolling--requiring a slightly higher temperature (600°C instead of 500°C for 52100) before it can be rolled effectively.

Determination of a criterion that attempts to explain alligatoring in terms of roll-specimen geometry results in the variable, Δ . Δ is approximately an h/L ratio where h is equivalent to the average thickness of the specimen and L is roughly the chord of the arc of contact between roll and specimen. In this study, Δ is more precisely:

$$\Delta = (h_o/4Rr)^{1/2}(2-r)$$

where h_o = thickness of piece before rolling, R = radius of the rolls, and $r = (1-h_f/h_o)$ where h_f is the thickness of the piece after rolling. An important point to note here is that given a specific roll diameter, a small Δ corresponds to a large reduction for a particular pass.

Δ for the alligatoring of 1020 steel is the following: At room temperature, 1020 specimens alligator at approximately $\Delta = 2.5$. Warm-rolling at temperatures of 427°C and 500°C results in alligatoring at slightly lower values of Δ -- $\Delta = 1.0$ to $\Delta = 2.5$.

For UHC steel, Δ at the point of alligatoring is as follows: 52100 did not alligator above 500°C, though cold-rolled specimens of 52100 edge cracked very severely at $\Delta = 3.0$. On the other hand, 52150 alligated at 540°C with $\Delta = 2.5$ --in the same range as cold-rolled 1020.

Δ vs ϵ has been plotted for alligated 1020 steel (See Figure 1); and a few notable points can be observed from this resulting graph. Firstly, in cold-rolling, it appears that a critical region exists where alligatoring of the 1020 specimen takes place. The boundaries of this region extend from $\Delta = 1.75$ to $\Delta = 3.0$ and from $\epsilon = 0.8$ to

$\epsilon = 1.5$. Avoiding this critical region--for instance, by taking small (less than 1%) reductions in thickness per pass--would result in the prevention of alligating of the specimen (though some other failure mode such as edge cracking may take effect).

For 1020 at warm-rolling temperatures--427°C and 500°C-- the critical region is shifted to lower values of Δ ($\Delta = 1.0$ to $\Delta = 2.5$) and a slightly lower and wider range of ϵ ($\epsilon = 0.6$ to $\epsilon = 1.1$). Again, avoidance of this critical region by either taking small or very large reductions per pass would appear not to lead to alligating (but perhaps to some other failure mode--for instance, 'unzippering').

A small amount of data has been gathered for UHC steels in terms of Δ . 52100 edge cracks at roughly $\Delta = 3.0$ and $\epsilon = 0.6$; and no failure is encountered upon rolling at 500°C and higher. 52150 rolled at 540°C alligated at the same critical region as cold-rolled 1020--roughly $\Delta = 2.0$ to $\Delta = 3.0$ and $\epsilon = 0.8$ to $\epsilon = 1.3$. However, at 600°C and higher temperatures, no ill effects are noted.

C. DETERMINATION OF RESIDUAL STRESSES IN ROLLED STEELS

(Dr. Oleg D. Sherby; Simeon de Jesus III)

Residual stresses build up in materials that are subjected to heavy deformation--in this case, the rolling of 1020 and UHC steels. These stresses are sustained ('locked in') the rolled pieces, and are generally due to inhomogeneous volume or shape change.

By the theory of acoustoelasticity, a longitudinal wave passing through a solid deformed due to either applied or residual stresses propagates with a velocity, v , which is different from the velocity, v_0 , of the same wave moving through undeformed material. By this technique, an absolute scale of stresses is difficult to determine; though it is the relative frequency change with respect to the unstressed condition that is proportional to the stresses that exist within the deformed material.

The method of measuring residual stresses by acoustoelastic techniques is generally as follows: A longitudinal acoustic wave is directed normally on a flat sample surface--the sample having two such flat and parallel surfaces. Transit time measurements of front and

back side reflected waves can therefore be used to ascertain the state of stress in the deformed medium. Data are collected across samples of uniform thickness; and this information can then be related to the state of residual stress existing in the sample. This technique has the significant advantage of performing rapid, non-destructive evaluation of bulk residual stresses.

A major problem involves separating relative contributions of initial anisotropy and residual stress. Measured relative wave velocity changes can be induced by a variety of material properties in addition to stress--residual stresses exist in conjunction with inhomogeneous material properties. As a basis of comparison, the state desired for calibration would be the final state minus the residual stresses--leaving micro-structural effects of the specimen history intact. This state can be achieved by a 'stress relief' heat treatment where the specimen is heated to a temperature high enough to relieve a considerable amount of stress yet low enough to avoid excessive grain growth. Unfortunately, all of the residual stresses are rarely completely relieved by this treatment.

At the present, residual stress measurements by acoustoelastic techniques are being attempted on 1020 steels which have been rolled to an effective strain of $\epsilon = 1.0$ --a decrease in thickness from 2.0 inches to 0.82 inches. This corresponds to the point just before the material is expected to alligator.

D. A UNIFIED NUMERICAL METHOD FOR UTILIZING UNIFIED CONSTITUTIVE EQUATIONS IN FINITE-ELEMENT CODES (A. K. Miller and T. Tanaka)

In most present finite-element codes, the constitutive equations include separate, empirical, non-coupled equations for "time-independent plasticity" and "time-dependent creep". Satisfactory numerical methods are available, but one method (tangent modulus) must be used with the "plastic" strains and a different method (initial strain) must be used with the "creep" strains. (Figure 2A).

With the advent of unified, physically-based constitutive equations (e.g. MATMOD) which handle both the "plasticity" and "creep" together, serious numerical difficulties have arisen at a number of laboratories in utilizing these unified equations in finite-element

codes. (Figure 2B)

Accordingly, we have been concentrating our effort this year on developing a unified numerical method specifically suitable for unified constitutive equations (Figure 2C). Thus far, the new method has worked successfully for simple constitutive equations involving arbitrary combinations of strain hardening and strain-rate sensitivity. The same method works successfully and economically for one-dimensional cyclic deformation using the MATMOD constitutive equations, simplified to have $F_{sol} \equiv 0$. Thus the method appears quite promising for finite-element applications.

FIGURE 1

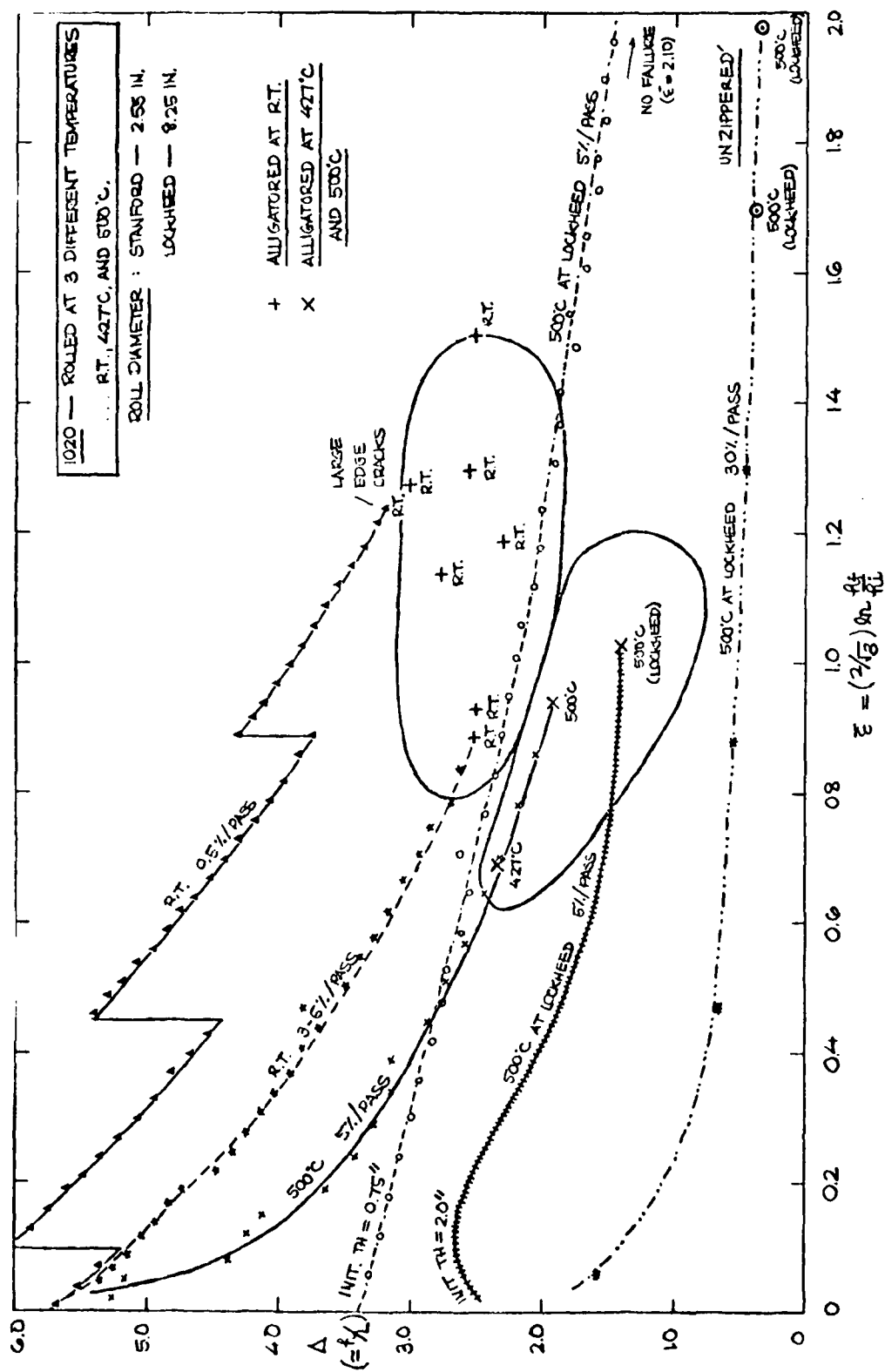


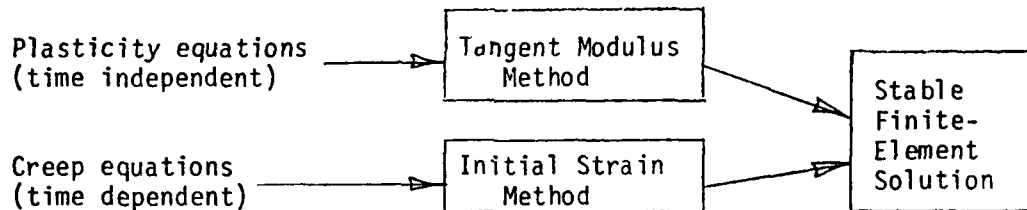
FIGURE 2

A UNIFIED NUMERICAL METHOD FOR
UTILIZING UNIFIED CONSTITUTIVE EQUATIONS
IN FINITE-ELEMENT CODES

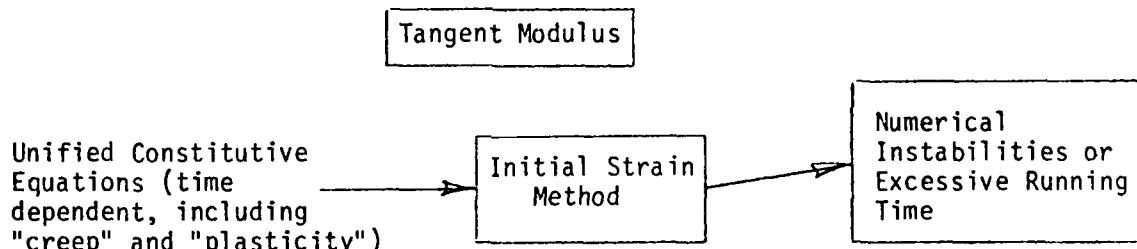
(T. Tanaka and A. K. Miller)

I. OBJECTIVE AND APPROACH

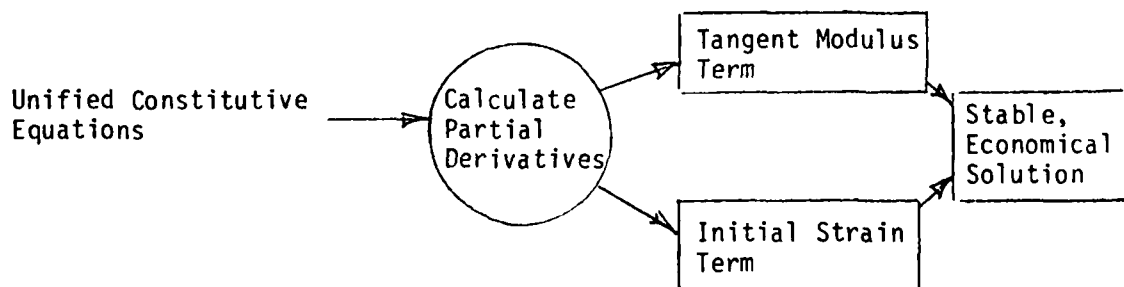
A. PRESENT METHODS OF ANALYSIS



B. PREVIOUS ATTEMPTS AT USING UNIFIED CONSTITUTIVE EQUATIONS



C. NEW UNIFIED NUMERICAL METHOD



SECTION C

INDIVIDUAL RESEARCH PROGRAMS

SECTION C

INDIVIDUAL RESEARCH PROGRAMS

1. ACOUSTIC AND MAGNETIC WAVES AND DEVICES

B. A. Auld, Adjunct Professor, Hansen Laboratories

Graduate Students:

S. Ayter
L. Gjaen
H. Kunkel
F. G. Muennemann
M. Riaziat*
M. Tan

*Received M.S. during report period.

Agency Support:

Battelle B-96062-B-K
DOE-Ames SC-81-011
EPRI RP-1395-3
Navy N00014-79-C-0222
Navy N00014-76-C-0632
NSF ENG 77-28541
Rockwell RISC B0-F01243-3
Rockwell B1-F000429-2
NSF-MRL through CMR - Thrust Program on Acoustic
Nondestructive Testing

Technical Objective:

To investigate acoustic and magnetic resonance and wave propagation phenomena and the use of new materials for device application in this area.

Research Report:

(1) Ferromagnetic Resonance Probe for Detecting Surface Flaws in Metals

Graduate Students: F. Muennemann and M. Riaziat

This work is in part related to a "Thrust" Program on Nondestructive Evaluation supported by the National Science Foundation's Materials Research Laboratory Program through the Center for Materials Research.

A new approach to microwave eddy current testing for surface cracks in metals involves the use of ferromagnetic resonance in a small yttrium iron garnet crystal placed close to the surface to be tested. It is well known that, in this situation, induced eddy currents on the metal surface cause a strong displacement of the ferromagnetic resonance

frequency. The presence of a crack on the surface produces, by disturbing the eddy current pattern, a perturbation of the garnet sample as it passes over the crack. Several models of such probes have been tested experimentally, demonstrating the principle.

During the past year our efforts have concentrated on the theory of these probes and on analysis of probe-flaw interactions. We have developed a theory of the response of the ferromagnetic resonance probe to both two- and three-dimensional surface cracks, in the limits of small and large values of the ratio crack dimension to material skin depth. This analysis shows that these probes, because they operate at very high frequencies, are much more sensitive to crack opening than are standard low-frequency eddy current probes. Because of this, they are ideally suited for studies of crack closure stress, an important topic in modern fracture mechanics.

(2) Quantitative Modeling of Flaw Responses in Eddy Current Testing

Graduate Students: M. Riazat and L. Gjaen

The general objective of this project is to develop the theory of eddy current flaw testing in metallic structures, using the reciprocity relation approach, and to apply this theory to the interpretation of results obtained by testing experimental models of flaws. One essential feature of the results obtained is a demonstration of the value of spatial frequency response in conceptualizing and designing eddy current probes. It has been shown both theoretically and experimentally that an eddy current probe can be designed as a spatial frequency filter to optimize the ratio between the signal obtained from a flaw and spurious signals derived from jitter and wobble of the probe as it is scanned over the sample.

We have also been formulating a variational approach to the eddy current problem. For typical flaw geometries interrogated with a non-uniform eddy current pattern, typical of practical probes, exact analysis of the field problem is not possible. At the present time we have developed a variational analysis suitable for the case of flaws that are large compared to the skin depth and we are applying this to a number of typical geometries.

(3) Interactions of Acoustic Waves With Domains in Ferroic Materials

Graduate Student: M. M. Fejer

The goal of this project is to study the nonlinear interaction of acoustic waves with domain walls in ferroic (ferromagnetic, ferroelectric and ferroelastic materials) with a view, first of all, of achieving a better understanding of the basic physics involved and of evaluating the potential of such applications for new device applications. In this project we are concerned especially with nonlinear interactions between acoustic waves and ferroelastic domain walls, i.e., (1) the effect of a domain wall on the nonlinear properties of the medium, (2) the influence of domain wall structures on acoustic (and optical) harmonic generation, and (3) the displacement of a domain wall or walls under the action of static forces generated by "rectification" of an acoustic wave. Initially, work focused on gadolinium molybdate (GMO) but more recently we have also begun to consider another ferroelastic, neodymium ultraphosphate (NUP). During the past year we have been: (1) studying the growth of single crystal GMO fibers by a laser melting technique, (2) fabricating composite LiNbO_3 -NUP resonators for experiments on acoustic-domain wall interactions, and (3) developing a laser probe method for measuring second harmonic generation in single crystal resonators, a technique aimed toward the measurement of nonlinear elastic constants in new crystal materials.

(4) Variational Analysis of Resonant Scattering of Acoustic Waves From Cracks and Slots in Plates

Graduate Student: M. Tan

This project is concerned with the application of variational techniques to the analysis of acoustic wave scattering from slots and discontinuities in plates, with particular emphasis on resonant scattering. The materials relationship of this program is through the potential interest of the results for nondestructive evaluation technology applied to ultrasonic flaw detection in plates. Two types of analysis have been developed for scattering from two- and three-dimensional cracks or slots in plates. Calculations have been made of scattering from two-dimensional cracks extending almost entirely through a thin plate. It

is found theoretically and confirmed experimentally that ultrasonic scattering from such large cracks can go to zero at a certain frequency determined by the crack dimensions. This phenomenon is due to a resonance effect involving waveguide modes.

(5) Acoustic Wave Scattering From Surface Cracks

Graduate Student: S. Ayter

The purpose of this project is to develop theoretical criteria for the detection and characterization of surface cracks and flaws in materials by means of Rayleigh wave scattering. From a materials point of view it may therefore be classified in the area of Materials Testing Techniques. One aspect of the problem under study is the use of mechanical resonance of a crack as a means for determining the dimensions of the crack or flaw. The experimental side of the program involves use of a laser probe to measure the distribution of elastic displacement in the vicinity of a flaw illuminated with an incident ultrasonic wave, in order to determine the spatial distribution of displacement corresponding to various resonances. A second part of the investigation deals with analysis of the effect of surface roughness and nonplanarity on the precision of crack sizing by ultrasonic scattering techniques. Two theories of elastic scattering from rough surfaces have been developed and these are being applied to the crack problem.

(6) Elastic Domain Wall Waves in Ferroelectric Ceramics and Single Crystals

Graduate Student: H. Kunkel

The purpose of this research is to investigate the use of new types of elastic waves as probes for examining the material properties of piezoelectric and electrostrictive types of ferroelectric ceramics and single crystals. The elastic waves to be considered have the character of being guided as interface waves along the domain walls in the ceramic (boundaries between regions of different electrical poling orientation) or of being trapped between pairs of domain walls. Samples of various classes of ferroelectric ceramics are prepared with different domain patterns and a technique has been developed using a laser probe

to measure the distribution of electrical polarization, static strain and elastic wave vibration in the vicinity of the poling transition regions.

Reference Publications:

1. M. Tan and B. A. Auld, "Normal Mode Variational Method for Two- and Three-Dimensional Acoustic Scattering in an Isotropic Plate," Presented at the 1980 Ultrasonics Symposium, Boston, Massachusetts (November 1980).
2. B. A. Auld and S. Ayter, "Perturbation Method for Analyzing the Effect on Ultrasonic Echo Returns on Rough Surfaces in Material Cracks and Voids," Presented at the 1980 Ultrasonics Symposium, Boston, Massachusetts (November 1980).
3. B. A. Auld, F. Muennemann, and D. K. Winslow, "Observation of Fatigue Crack Closure Effects With the Ferromagnetic Resonance Eddy Current Probe," J. Nondestructive Evaluation (accepted for publication).
4. B. A. Auld, "Ferromagnetic Resonance Flaw Detection," Physics in Technology (to appear, July 1981).

2. DEFORMATION IN SOLIDS

D. M. Barnett, Professor, Materials Science and Engineering and (jointly)
Division of Applied Mechanics (Mechanical
Engineering)

Graduate Students:

L. A. Gore*
M. P. Scott*
E. G. Tolf
C. Jackson

*Received PhD during report period.

Agency Support:

EPRI RP 609-1
AFOSR 2-DJA-786
NSF-MRL through CMR - Thrust Research Program on Acoustic
Non-Destructive Testing

Technical Objectives:

- (1) To use ultrasonics for the quantitative non-destructive determination of residual stress states in metals.
- (2) To develop improved collocation and boundary integral equation methods for performing stress analysis in solids containing cracks.

Research Report:

1. Non-Destructive Acoustic Determination of Residual Stresses

Graduate Students: M. P. Scott (Ph.D. received 12/80)
C. Jackson

The complete pointwise state of residual stress in aluminum billets hydrostatically extruded to area reductions of about 25% has been obtained by measuring relative longitudinal acoustic wave velocity shifts across the extruded samples. This technique for residual stress determination is non-destructive in nature, is fully automated, and is extremely rapid. In the past year we have developed a scanning acoustic system which uses acoustic shear waves to give us the capability of studying residual stress states which are more complicated than the axis-symmetric states associated with hydrostatic extrusion. Measurements of relative shear wave velocity shift as a function of shear wave polarization on

tensile coupons cut at various directions to the rolling direction from rolled aluminum plates show that there exists a marked influence of specimen initial anisotropy on the shear wave data. It appears as if there is significant information which can be obtained from shear wave scanning of stressed samples, and, in the coming year, these types of experiments will be used to study stainless steel samples under stress as well as regions near welds in samples sectioned from welded pipes and plates.

2. Stress Analysis of Cracked Solids

E. G. Tolf (Fulbright Exchange Scholar)

A rather powerful technique for performing stress analysis in cracked solids is based on the solution of integral equations. Two types of integral equations may be formulated to treat such problems, namely, integral equations arising from distributions of dislocations and integral equations based on point force distributions (the classical boundary integral methods). It is not clear for which class of problems one or the other of these methods is most suitable. In the area of acoustic non-destructive testing, an important laboratory tool is the interaction of surface acoustic waves with edge cracks. In order to approach this class of problems we have begun by re-examining the oft-studied problem of an edge crack in a semi-infinite medium subjected to remote uniaxial tension. Most previous numerical treatments of this problem are in error because of inappropriate assumptions about the behavior of the elastic fields of the crack near the trailing edge (at the free surface). In the surface wave-crack problem a proper treatment near the free surface is absolutely essential. We have developed a new collation technique which properly accounts for the correct trailing edge condition in the static problem and, during the coming year, will explore the suitability of the method for the surface wave problem.

Reference Publications:

1. M. P. Scott and D. M. Barnett, "The Non-Destructive Determination of Residual Stress in Extruded Aluminum Billets Using Acoustoelastic Methods", (in preparation).
2. E. G. Tolf, G. Wong, and D. M. Barnett, "An Improved Collection Method for Solving Edge Crack Problems (in preparation).

3. PHOTOELECTRONIC MATERIALS PHYSICS

Clayton W. Bates, Jr., Professor, Materials Science and Engineering and
Electrical Engineering

Professional Associates:

G. K. Wertheim	Bell Labs, Murray Hill, New Jersey
J. B. Mooney	SRI International
R. Lamoreaux	SRI International
H. R. Allcock	Pennsylvania State University
M. Uekita	Visiting Scholar

Graduate Students:

S. A. Raza	Received Master's degree during report period
K. Nelson	
C. Abernathy	
M. Jordan	
C. Y. Kao	
Y. S. Kim	

Agency Support:

NSF-MRL through CMR
NSF -ECS-7909453
SERI Subcontract XS-9-8104-4

Technical Objectives:

The objectives here are to investigate the structural, electronic and optical properties of crystalline and amorphous materials and to correlate these properties with their photoelectronic behavior. Recent studies have been concerned with low work function surface layers sensitive to visible and infrared radiation (photoemitters) and semiconducting compounds for use in solar cells.

Approach:

The photoelectric yield over a wide electron energy range is studied and related to such properties as the bandgap and other material parameters for the photoemissive surfaces. X-ray photoelectron spectroscopy (XPS) is currently being used to explore valence bands, charge states of elements in complex systems, and stoichiometry.

Optical absorption, Hall Effect, and resistivity measurements complement the XPS studies on the solar cell materials.

(1) XPS Study of Ag-O-Cs

The Ag-O-Cs or S-1 photocathode is unique among photoemissive materials with useful sensitivity to visible light. It was the first, and for many years the only, cathode available for practical applications. Because of its useful response in the visible and near infrared region of the spectrum, it continues to find widespread use in many photoelectric applications. In spite of this no explanation of the observed quantum yield in this spectral region has been previously given that is consistent with the experimental results on this surface, since it was discovered fifty years ago. Only recently has the chemical composition been established in detail.

The generally accepted structure of the S-1, obtained from many studies over the years and before this work was undertaken, consisted of silver particles up to about 200Å in linear dimensions approximately spherical in shape, and distributed throughout a matrix 200-400Å thick with a stoichiometry determined to be close to Cs_2O . This picture, however, does not provide an explanation for the 1.2μ threshold, and only a highly speculative explanation for the yield between 4000 and 9000Å has been provided.

X-ray photoelectron spectra of Ag, O, and Cs and quantum yield distributions from surfaces prepared by evaporating Cs onto Ag oxidized in ultrahigh vacuum have been measured. The structure of this surface determined from these measurements consists of silver particles dispersed in a matrix of Cs_2O with a layer of Cs_{11}O_3 on top. The threshold at 1.2μ is due to a lowering of the surface barrier by the Cs_{11}O_3 and the yield in the visible and near infrared is explained as due to the excitation of Mie or optical resonance absorption in the silver particles.

In the present experiments we varied the angle of observation of the photoemitted electrons, and from a measurement of the areas and the published data for photoionization cross sections, established that the Cs_{11}O_3 exists as an overlayer on Cs_2O . In another series of experiments on the oxidation of cesium in ultrahigh vacuum on various substrates we

found the same general behavior, i.e., Cs_{11}O_3 is produced along with Cs_2O as an overlayer on Cs_2O . These experiments further indicate that after a "certain" thickness of Cs_{11}O_3 is grown cesium peroxides begin to form upon further oxidation. This is noted as a shift of the 01s peak at 531.5eV to 530eV and a gradual attenuation of the Cs_2O 01s peak at 527.5eV. This layer of Cs_{11}O_3 appears to form over a narrow range of oxygen exposures and from varying the angle of observation of the photoemitted electrons we estimated this layer to be 10 - 20Å over a Cs_2O layer ~40Å thick. This provides an explanation for why Ebbinghaus et al. in their ultraviolet photoelectron spectroscopy work on oxidized cesium only detected Cs_{11}O_3 . The HeI resonance line at 21.2eV would only sample electrons from a depth of a few angstroms.

The enhanced yield of the silver particles is another matter. Just recently A. Schmidt-Ott and coworkers observed an enhancement of the photoelectric yield if ultrafine silver particles with radii 50Å are used as photoemitters. The system obeyed the Fowler-Nordheim law $Y = C (h\nu - \phi)^2$ for $(h\nu - \phi) \geq 1.5\text{eV}$. They noted that the yield for particles 20Å in diameter was a factor of 110 over that for a macroscopic smooth surface of silver. ϕ changes by a very small amount so it does not enter into the description of the phenomena. Resonance absorption of radiation by small metal particles suspended in a dielectric has been known for many years and was obtained from a theory developed by Maxwell-Garnet for small metal particles dispersed in a dielectric or, in the limit of small isolated spheres, from Mie scattering theory. Provided the small metal particles and their separations are much smaller than the wavelength of the incident light, this resonance or Mie absorption corresponds to the collective absorption of the metal particles much like plasma resonance. The resonance wavelength λ_R is strongly dependent on the density of the metal clusters, the ambient dielectric constant, and the presence of nearby interband transitions as indicated by the following equation given by Moskovits

$$\lambda_R = \lambda_p \left[1 + \frac{b}{a} \left(\frac{2+q}{1-q} \right)^{1/2} \right]^{1/2}$$

In equation (1) λ_p is the plasma wavelength for the metal, ϵ_b the interband contribution to the complex dielectric constant of the metal, and q is the volume fraction of the metal within a dielectric of dielectric constant ϵ_o . Though this simple expression does not give the details of the variation of λ_R with the particle size specifically (this is somehow related to q) it suffices for our interpretation of the photoyield of S-1 surfaces in the visible and near infrared. The model for which this expression was derived, i.e., small particles with linear dimensions $\ll \lambda$, the incident wavelength, suspended in a dielectric, is a good approximation to the structure of S-1 photocathodes. For silver, ϵ_b is approximately a constant in the visible region of the spectrum equal to 4 and λ_R is 1360Å. Assuming a value of $\epsilon_o = 3$ for Cs_2O and 0.75 for q , λ_R is 8000Å. For small values of q , λ_R occurs at shorter wavelengths and for large values, λ_R is in the red. Thus λ_R is a function of the specifics of the particle size distribution and their volume content in the dielectric. These numbers are presented to show that reasonable values for the parameters involved in the determination of λ_R give the experimentally observed λ_R .

The reason that silver works better than any other metal is a reflection of the fact that it forms small spherical agglomerates in thin films and the optical constants of silver as a function of wavelengths (ϵ_b is large due to a d-s transitions) place λ_R in the visible to near infrared. Other materials such as Cu with $\epsilon_b = 10.9$ and Au with $\epsilon_b = 8.2$ should absorb better in the infrared if a matrix could be found with a relatively small bandgap where the Fermi level of the metal and matrix would be $< 1.0\text{eV}$ from the conduction band minimum of the matrix.

This work gives, for the first time a structure for this surface that is consistent with the results of previous experiments performed on this system. More importantly it suggests a means of "tailoring" the spectral response of this surface by using Cu, Au, and/or Ag as described above, the first time such a result has been obtained for practical photocathodes.

(2) XPS Studies of Superficially Oxidized Cesium Antimonide Photoemitters

Professional Associate: G. K. Wertheim

Superficially oxidized cesium antimonide photoemitting surfaces prepared in ultrahigh vacuum were studied by x-ray photoelectron spectroscopy. Oxidation of Cs_3Sb to produce a surface with enhanced photosensitivity converts part of the antimony to elemental antimony and part of the cesium to cesium suboxide. The latter is identified on the basis of an $\text{O}1\text{s}$ peak at 531.3eV, characteristic of Cs_{11}O_3 . The production of Cs_2O is not ruled out in this process since its signature at 527.5eV is masked by an antimony shake-up peak at 527eV.

Our studies suggest that the production of Cs_{11}O_3 by the superficial oxidation of Cs_3Sb is responsible for the reduction in work function which increases the response to all wavelengths. It more than compensates for the destruction of the Cs_3Sb . The excess antimony is released as elemental Sb. We do not rule out the possibility that Cs_2O and other compounds of Sb are also produced. Further oxidation results in the production of more Cs_{11}O_3 with an increase in the long-wavelength threshold and a decrease in the sensitivity at shorter wavelengths. It is suggested that the oxidation effects are felt later by the slower electrons excited by longer wavelengths, because the faster electrons do not benefit to the same degree from the lower surface barrier. Continued oxidation eventually destroys most of the Cs_3Sb film, resulting in a layer of Cs_{11}O_3 on a substrate hardly recognizable as Cs_3Sb .

(3) Structural, Thermodynamic, and Electronic Studies of CuInSe_2 and CdS Films for Solar Cell Applications Prepared by Spray Pyrolysis

Graduate Students: A. Raza, Kim Nelson

Professional Associates: J. B. Mooney, R. Lamoreaux, M. Uekita

This program was initiated with the major objective of the preparation of a solar cell using spray pyrolysis for the deposition of all but the contact metalization, and having the structure glass/Au grid/p-CuInSe₂/n-CdS/Al.

Thin films ($\sim 1\mu$) of CuInSe_2 and CdS have been prepared by spray pyrolysis. The component ratios in the spray solutions and the glass substrate temperature were varied in order to produce films of the desired stoichiometry. The importance of the starting ratio for both CuInSe_2 and CdS was demonstrated. The optimum spray conditions were suggested by thermodynamical calculations using a free energy minimization computer program applied to the Cu-In-Se system. Optical absorption studies of films verified the existence of the proper compound.

Heat treatment of the films were performed in order to produce conductivities and crystal structures for photovoltaic applications. In particular for CuInSe_2 which gives the sphalerite structure under most spray conditions, a short heat treatment of 10 minutes at 600°C is described which produces the chalcopyrite structure. Most recently we have produced films of CdS doped with indium that have resistivities of $1\ \Omega\text{-cm}$. These films appear to be quite stable in air and require no heat treatment. We have also been successful in producing the chalcopyrite structure directly for CuInSe_2 with a starting ratio of Cu:In:Se of 1.2:1:4. However, more work needs to be done on this system as various heat treatments in nitrogen causes a conversion to the sphalerite structure.

(4) XPS Studies of Polyphosphazene Polymers

Professional Associate: H. Allcock

We have made the first XPS studies (including the valence band) on the first synthesized carborane-substituted phosphazene linear high polymers.

These species are prototypes for a wide range of carborane-phosphazene rings and polymers that are of broad theoretical and practical interest. No electrical or optical studies have been made on these materials to date. As these polymers can withstand temperatures of 450°C without serious material degradation, they may find widespread use as heat shield materials in space applications for extraterrestrial vehicles, uv stable coatings, and aircraft seating materials.

The data from the XPS measurements have not been analyzed in detail but they do indicate that the stoichiometry is close to the predicted chemical formula. A surprising result of these studies is that the structures containing approximately 15% of the side groups as carboranyl units appear to be unstable under prolonged x-ray excitation.

List of Materials-Related Publications Since Last Report

1. C. W. Bates, Jr. and L. E. Galan, "X-Ray Photoemission and Auger Electron Spectroscopy of Multialkali Antimonide Photocathodes", Proceedings of the 9th International Symposium on Photon Detectors of the International Measurement Confederation, Vol. I, 100-129 (1980)
2. L. Galan and C. W. Bates, Jr., "Structure of Multialkali Antimonide Photocathodes Studied by X-Ray Photoelectron Spectroscopy" J. Phys. D: Appl. Phys. 14, 293 (1981)
3. C. W. Bates, Jr. "Concepts and Implementations in X-Ray Image Intensification ASTM STP 716, 45 (1980)
4. C. W. Bates, Jr. et al, "X-Ray Photoemission Studies of Superficially Oxidized Cesium Antimonide Photoemitters", Appl. Phys. Lett. 38, 387 (1981)
5. C. W. Bates, Jr. et al, "Spray Pyrolysis and Heat Treatment of CuInSe₂ and CdS for Photovoltaic Applications", accepted for publication in J. Thin Solid Films
6. C. W. Bates, Jr., "Photoemission from Ag-O-Cs, accepted for publication in Phys. Rev. Lett.

4. SUPERCONDUCTIVITY

M. R. Beasley, Professor, Applied Physics and Electrical
Engineering

Professional Associates:

T. W. Barbee, Jr.
R. H. Hammond
B. Pannetier

Graduate Students:

L. H. Allen
S. J. Bending
M. S. Di Iorio
J. M. Graybeal
A. J. deLozanne
T. P. Orlando
D. A. Rudman
S. T. Ruggiero (Received Ph.D. during report period.)

Agency Support:

DOE DE-AT03-76ER71043
JSEP N00014-75-C-0632
N00019-79-C-0618
NSF DMR79-11117
NSF-MRL through CMR - Thrust Program on Noncrystalline Metals

Technical Objective:

To extend and deepen the understanding of the electromagnetic behavior of superconductors of superconducting structures and devices

Approach:

The response of superconductors to currents, magnetic fields, and electromagnetic radiation under a wide variety of conditions are studied and related to the basic properties, structure, material parameters, and geometry of the superconductors. Tunneling studies of high- T_c superconducting materials to determine microscopic electronic properties of superconductors and to explore device possibilities.

Studies of two-dimensional phase transitions as manifest in superconducting thin films and layered structures.

(1) Superconducting Tunneling and Tunneling Applications in High- T_c Al5 Superconductors

Graduate Student: D. Rudman

Tunneling junctions exhibiting both quasiparticle and Josephson tunneling are being made on the high- T_c Al5 superconductors deposited by means of electron beam coevaporation. The junctions have been found to be superior to any obtained previously and are making possible detailed study of the basic electronic properties (e.g. energy gaps Δ and electron phonon spectral function $\alpha^2F(\omega)$) of these superconductors. Josephson device potential is also being investigated. During the past year we have been applying these junctions to a detailed understanding of $\alpha^2F(\omega)$ as a function of composition.

These recent studies suggest that for Nb_3Sn as one approaches stoichiometry (i.e. the highest T_c material) not only is there an overall increase in the strength of $\alpha^2F(\omega)$ but an increase weight at low frequencies. This last feature has also been seen by J. Kwo in Nb_3Al . These results relate directly to the details of the origin of the superior superconducting properties of these materials and possibly the relation of superconductivity to lattice instabilities. Unfortunately the analysis required to extract such information from the tunneling that is subject to corrections required to account for both an apparent region of depressed superconductivity at the sample surface (i.e. the proximity effect) and strong variations in the band density of states near the Fermi energy that are present in some of these Al5 superconductors. The nature and quantitative importance of these corrections needs to be critically assessed before final conclusions can be made.

(2) High- T_c Superconducting SNS Microbridges

Graduate Students: A. de Lozanne and M. Di Iorio

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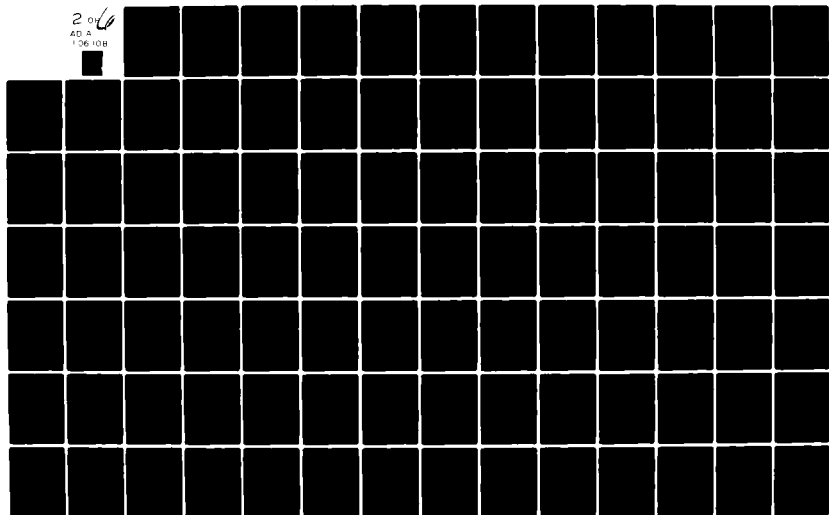
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The objective of this project is to make SNS planar microbridges incorporating high- T_c superconductors. Our previous work has shown that the high- T_c materials are extremely sensitive to damage during processing. To alleviate these problems we have developed a plasma etching process that can successfully form small ($\sim 0.3 \mu\text{m}$) SNS bridges with no apparent damage (e.g. reduction of T_c).

These techniques have now been successfully applied to Nb/Au/Nb SNS bridges. The electrical behavior of these devices (critical currents and I-V curves) are found to be in accord with existing theories providing that a more realistic model of the S/N and bridge/bank interfaces were introduced.

More recently, extensions of these techniques and incorporation of a step edge in the substrate to define the bridge length has led to the successful fabrication of a high- T_c , $\text{Nb}_3\text{Sn}/\text{Cu}/\text{Nb}_3\text{Sn}$ SNS Josephson device with a large ($\sim 1 \text{ mV}$) $I_c R_N$ product and an operating temperature range of 2 K to 16.5 K. This is the first demonstration of a high- T_c Josephson device whose operating temperature range is not restricted to a very narrow temperature interval near T_c .

(3) Superconducting Layered Structures and 2-D Superconductivity

Graduate Students: S. Ruggiero and J. Graybeal

We have been studying the electric and magnetic behavior of finely (8 \AA to 100 \AA) layered periodic SNS composites formed by vapor deposition. These are of interest because of the information they provide about SN interfaces and because of the novel superconducting properties expected in Josephson coupled 2-D systems. With these systems we have unequivocally observed the 3-D to 2-D dimensional crossover predicted for layered superconductors as the temperature is reduced below T_c . This novel crossover is different from those commonly seen in lower dimensional systems in the fluctuation regime above the phase transition temperature. The crossover observed in superconductors manifests itself in a dramatic increase in the critical magnetic field and critical current of the superconductor (in parallel magnetic fields) when the coherence length becomes comparable to the layer separation as

the temperature is decreased. Excellent quantitative agreement with theory is obtained. We have also extended our measurements to include the fluctuation conductivity above T_c where dimensional crossover behavior is also seen. These data are also in accord with available theory using material parameters consistent with those deduced from the critical data below T_c . Finally we observe an anomalous temperature dependence in the perpendicular critical fields. Such behavior has been reported previously in the layered compound superconductors. Its presence in these more ideal artificial systems strengthens the evidence that this anomaly is intrinsic to quasi-two-dimensional superconductors and not due to sample imperfections.

(4) Critical Fields of AlS Superconductors

Graduate Student: T. P. Orlando and S. Bending

As we have previously reported the upper critical field behavior of Nb_3Sn and V_3Si are being studied as a function of disorder (as measured by residual resistivity) and the results analyzed within the framework of the GLAG theory including the effects of the electron-phonon interaction. A surprising conclusion of this study is that the apparent absence of Pauli paramagnetic limiting in clean Nb_3Sn and by contrast its presence in clean V_3Si results significantly from the stronger electron-phonon interaction in Nb_3Sn . In the past this has been attributed to a large spin-orbit scattering rate. The present materials are too clean for this to be possible. We have developed a simple physical argument showing that the electron-phonon interaction increases the Pauli limit above the BCS value, thus decreasing the required spin-orbit scattering. These corrections have heretofore been neglected in analyzing the behavior of high field superconductors although it is now clear that they are implicit in the usual theory. Neglect of these corrections in analyzing real data is a major oversight since such corrections are non-negligible even in relatively weak coupled superconductors. This fact also appears not to have been appreciated previously.

More recently we have extended this study to include an analysis of the critical field data of V_3Ga . In this case the observed $H_{c2}(0)$ is too low, necessitating the introduction of another many body correction, the electron-electron interaction and its associated Stoner factor and spin fluctuations. Indeed using critical field data it is possible to estimate that $S > 2$ in V_3Ga which is large enough to not only affect H_{c2} through the Pauli limiting mechanism but also T_c itself through the role of spin fluctuations. This last conclusion is rather startling given that V_3Ga is already a high- T_c material. These results can be shown to be consistent with the material parameters of V_3Ga more broadly.

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5. "Superconductivity in Quasi-Two-Dimensional Layered Composites," by S. T. Ruggiero, T. W. Barbee, Jr., and M. R. Beasley, *Phys. Rev. Lett.* 45, 1299 (1980).
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9. "The Microscopic Superconducting Parameters of Nb_3Al : How Important is the Band Density of States?", by J. Kwo, T. P. Orlando and M. R. Beasley, to appear in Phys. Rev.
10. "S-N-S Microbridges: Fabrication, Electrical Behavior and Modeling," by R. B. van Dover, A. de Lozanne and M. R. Beasley, submitted to Journal of Applied Physics
11. "Properties of High-T SNS Microbridges," by A. de Lozanne, M. Di Iorio and M. R. Beasley, to be presented at the LT-16 Conference, Los Angeles, California, August 1981.

5. STRUCTURES OF AMORPHOUS MATERIALS AND SYNCHROTRON RADIATION

A. I. Bienenstock, Professor, Materials Science & Engineering and
Applied Physics

Professional Associate:

J. Stöhr

Graduate Student:

S. M. Brennan

Agency Support:

NSF-DMR 73-07692 (SSRL)

NSF-DMR 79-08554

NSF-INT 77-06310

EXXON unrestricted grant

Technical Objectives:

To investigate atomic arrangements in amorphous materials in an effort to understand thermal, crystallization, electronic and vibrational properties. To determine atomic arrangements at the surfaces of materials. To develop synchrotron radiation techniques and instrumentation.

Approach:

The methods used during the past year were X-ray diffraction and extended X-ray absorption fine structure analysis.

Research Report:

(1) Photoemission and EXAFS Studies of Adsorbates and Surface Structure

Professional Associate: J. Stöhr

Graduate Student: S. Brennan

Research during the past year has been directed in two areas, photoemission from core levels of clean Si¹ and surface EXAFS of C(2x2)S on Ni(100)². In the photoemission work, binding energy shifts of the 2p core level were measured for a freshly cleaved Si(111) surface. Immediately after cleaving, extra peaks were visible at both higher and lower binding energy than the main split peaks. The extra peaks are attributed to those surface atoms involved in buckling into a (2x1) reconstructed surface. They disappeared when the surface was

exposed to oxygen, so that they could be attributed to surface atoms. These results should be of importance to workers calculating total surface energies or the size of the buckling on the surface.

The second area of experimentation was a continuation of earlier work on surface EXAFS of low-Z adsorbates, but utilizing a new SSRL monochromator which covers the spectral range from 850 to 4200 eV. This monochromator made accessible the absorption edges of the technologically interesting third row elements.

One of the most important catalyst poison systems is sulfur on nickel. It was felt that this system was a good candidate for further studies using surface EXAFS. While surface EXAFS had been used previously to study surfaces, the full potential of polarization dependent surface EXAFS on K-edges had not been realized. This polarization dependence allows the determination of the absorption site geometry, not merely the first neighbor distance. Due to the very good signal-to-noise achievable in surface EXAFS, a second shell distance was seen, which confirmed the absorption site. Accuracies attainable for near neighbor distances in surface EXAFS are better than $\pm 0.02\text{\AA}$, whereas previous LEED work had achieved accuracies of $\pm 0.06\text{\AA}$ in the first shell distance. With this work, surface EXAFS is shown to be the technique of choice for the determination of adsorption site geometries, especially for cases where the adsorbate causes disordering of the surface.

(2) Structural Studies of Amorphous Materials

Most of our research, which is devoted to structural studies of and electron-hole recombination in amorphous materials, is described in the section devoted to the Thrust Program on Metastable Materials.

Reference Publications:

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2. S. Brennan, J. Stöhr and R. Jaeger, "Structure Determination of C(2x2)S on Ni(100) using Polarization Dependent Surface EXAFS," submitted to Phys. Rev. Letters.
3. J. Stöhr, L. I. Johansson, S. Brennan, M. Hecht and J. N. Miller, "A Surface Extended-X-Ray-Absorption-Fine-Structure Study of Oxygen Interaction with Al(111) Surfaces," Phys. Rev. B 22, 4052 (1980).
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10. J. Stöhr, K. Baberschke, R. Jaeger, R. Treichler and S. Brennan, "Orientation of Chemisorbed Molecules from Surface Absorption Fine Structure Measurements: CO and NO on Ni(100)," submitted to Phys. Rev. Letters.

6. PROPERTIES OF ADSORBENTS AND CATALYSTS

M. Boudart, Professor, Chemical Engineering and Chemistry

Professional Associates:

J. E. Benson
G. Marin
R. A. Dalla Betta
T. Yoneda
Xiao-Hong Kang
Jae Eui Yie
R.C. Everson

Graduate Students:

W. G. Borghard
W. Cheng
W. Holstein
S. Ichikawa
E. Iglesia
M. McDonald
G. Meitzner (on leave)
T. Oyama*
J. Sanchez
L. Volpe**
R. Weber
G. Zhang

* Received PhD during
report period.

** Received MS during report period.

Agency Support:

NSF DMR 77-24222	NSF DAR 79-10071
NSF ChE 77-22722	DE AS03-76 SF 00326
NSF ChE 77-15385	NSF ENG 79-09141
NASA NCA20R-745-908	
Exxon Research and Engineering Company	
NSF-MRL through CMR - Thrust Program on Alloy Catalytic Materials	

Technical Objective:

To prepare and characterize finely divided materials and understand their chemical surface reactivity and catalytic activity in selected reactions.

Approach:

For the rational synthesis of catalytic materials, the physical chemistry of their preparation and of what follows it, namely the genesis of the catalyst, is studied by means of Infra-Red Absorption Spectroscopy (IRS), electron spin resonance (ESR), Mössbauer spectroscopy (MES), Auger electron spectroscopy (AES), X-ray diffraction (XRD), X-ray scattering (XRS), X-ray absorption (XRA), extended X-ray absorption fine structure (EXAFS), magnetic susceptibility measurements as well as conventional methods of physisorption, chemisorption and chemical reactivity including catalytic tests. The same methodology is applied to the structural and electronic characterization of the new materials, the final aim being an understanding of their catalytic activity and selectivity in a number of reactions.

Research Activity:

1. The Adsorption and Catalytic Oxidation of Carbon Monoxide on Evaporated Palladium Particles

Palladium crystallites, evaporated in UHV on a $\alpha\text{-Al}_2\text{O}_3$ single crystal support and characterized by transmission electron microscopy (TEM), have been used as catalysts for the low pressure oxidation of carbon monoxide between 450 and 550 K. Average particle diameters varied between 1.5 and 8 nm. The turnover rate N , i.e., the number of molecules of CO_2 made per second per surface palladium atom was measured. The number of surface palladium atoms was determined by combining TEM and temperature programmed desorption of CO. Values of N , under constant conditions, were practically identical on all samples. It is noted that the reaction studied is structure insensitive on palladium.

2. Hydrogenolysis of Carbon and its Catalysis by Platinum

The hydrogenolysis of carbon to methane and its catalysis by platinum were studied above and below 1050 K respectively. Hydrogen pressure varied between ca. 10 and 100 kPa. At 890 K and atmospheric pressure, platinum accelerated the rate of the uncatalyzed reaction by

a factor of 2000. Reaction orders with respect to H_2 and kinetic isotope effects in H_2 and D_2 suggest rapid equilibration of the carbon surface with hydrogen followed by a rate-determining step involving breaking of a carbon-carbon bond. This step appears to be a true hydrogenolysis step with direct participation of hydrogen in the uncatalyzed reaction. But with platinum, the rate-determining step seems to lead to the formation of a carbon-platinum bond with subsequent reaction of the carbidic carbon on platinum.

3. Catalytic Hydrogenation of Cyclohexene. The Effect of Sulfur on Supported Platinum

The rate of turnover r_t for the gas-phase hydrogenation of cyclohexene on platinum catalysts in the absence or the presence of sulfur was measured at 273K and pressures of H_2 and C_6H_{10} equal to 9.31 and 2.66 kPa. If the number of Platinum sites is measured by means of hydrogen chemisorption, r_t is found to be the same for all catalysts and equal to $0.65\ s^{-1}$ if it is assumed that one site corresponds to one hydrogen adatom. By contrast, if the number of platinum sites is measured by means of oxygen chemisorption or dihydrogen titration of prechemisorbed oxygen, r_t is constant only for the catalysts which are not contaminated by sulfur. For the others, values of r_t scatter depending on the amount of sulfur on platinum. It appears that adsorbed sulfur takes up oxygen, thus leading to excess values of the number of platinum sites. The constancy of r_t measured by hydrogen chemisorption on platinum with or without sulfur confirms the structure insensitivity of cyclohexene hydrogenation on that metal and the adequacy of hydrogen chemisorption as a method of counting platinum sites.

Reference Publications:

1. S.Ladas, H.Poppa and M.Boudart, "The Adsorption and Catalytic Oxidation of Carbon Monoxide on Evaporated Palladium Particles", Surface Science 102 (1981) 151-171.

2. W.L. Holstein and M.Boudart, "Hydrogenolysis of Carbon and its Catalysis by Platinum", submitted to the Journal of Catalysis.
3. G. Leclercq and M.Boudart, "Catalytic Hydrogenation of Cyclohexene. The Effect of Sulfur on Supported Platinum", accepted by the Journal of Catalysis.

7. PRIMARY PHOTOCHEMISTRY OF PHOTOSYNTHESIS

S. G. Boxer, Assistant Professor, Chemistry

Graduate Students:

R. R. Bucks
C. E. Chidsey
A. Kuki
E. F. McCord
R. S. Moog
M. G. Roelofs
K. A. Wright

Agency Support:

NIH GM-27738-01
NSF-MRL through CMR
NSF PCM 7926677
USDA 78-59-2066-0-1-147-1
DOE DE-FG02-CS84006

Technical Objective:

To obtain an understanding of the mechanism of the primary photochemical events of photosynthesis. Specific objectives include elucidation of the origin of the efficiency of the forward reaction (nearly 100%), the mechanism of stabilization of separated charge for times up to tens of nanoseconds, the generation of triplet excited states by anion-cation annihilation and the fabrication of artificial molecular systems which simulate these properties.

Approach:

This problem is approached along several convergent paths. (1) The synthesis of molecular aggregates which contain the molecules known or suspected to participate in the primary photochemistry. (2) Investigation of the fundamental spectroscopic properties of the chlorophylls and the nature of chlorophyll-protein interactions using synthetic chlorophyll-protein complexes. (3) The use of large magnetic fields to selectively perturb spin-dependent reactions as a means to provide detailed kinetic and magnetic information about photosynthetic reaction centers. (4) The development of high-field, high-resolution nuclear magnetic resonance methods to study laser induced photochemical

reactions involving biological macromolecules.

Research Report:

(1) R. R. Bucks - A large series of molecules has been synthesized which bring together the molecular constituents which participate in the primary photochemistry of photosynthesis. These include singly linked dimers and trimers, prepared from metal containing and metal free chlorophylls, and doubly linked cofacial analogues. Variables include redox potential, distance and solvent dielectric. The photophysical properties of singly linked arrays have been extensively investigated using ps absorption (3-5000 ps) and fluorescence (100-10,000 ps, using synchrotron radiation) in a search for charge transfer. Evidence for charge transfer is found when the potential of the electron donor excited state is more than 300 mV above the acceptor.

(2) K. Wright, A. Kuki, and R. Moog - The first well-defined 1:1 complexes between chlorophyll and a protein have been prepared by replacing heme in myoglobin and hemoglobin with a series of chlorophylls. We call these green proteins the chloroglobins. These complexes have been studied in detail as a model for chlorophyll-protein interactions. Solution studies reveal several subtle effects of the chromophore on conformational equilibria in the protein. Monomers, dimers and tetramers with defined 3-dimensional structure have been prepared and investigated by time-resolved fluorescence depolarization. Well-formed crystals of these complexes have been prepared which provide, for the first time, fully oriented chlorophylls for spectroscopic investigation. The orientations of transition dipole moments have been determined using a microspectrophotometer. These protein crystals offer a new type of material in which the chromophores can be viewed as constituting an oriented gas with unique site-substitution in a lattice.

(3) C. Chidsey and M. Roelofs - We have discovered that the triplet yield in reduced photosynthetic reaction centers can be perturbed in a well-defined way by the application of large magnetic fields. At low field the field lifts the degeneracy between singlet

and triplet radical ion pair energy levels and at high field it enhances the frequency of singlet-to-triplet conversion, by increasing the difference in resonance frequency of the radicals. The yield changes by as much as 400% between 0 and 50 kG. This result is interpreted as direct evidence for a difference in the g-factors of the primary radical ions in photosynthesis. A detailed theoretical analysis has been developed which yields the g-factor difference and the rate-constants for radical-ion recombination to the singlet ground and excited triplet states. This method should be generally applicable to studying ion-pair recombination in photosynthetic models or the analogous electron-hole pair recombination in amorphous semi-conductors.

(4) E. M. McCord - The 360 MHz nmr spectrometer at the Stanford Magnetic Resonance Laboratory has been modified to permit laser irradiation of the sample during the nmr experiment. During the past year this capability has been extended to include excimer laser excitation (249 or 308 nm). This opens up a wide range of new photoreactive molecules for examination by the technique of Chemically Induced Dynamic Nuclear Polarization. This method is being used to probe protein surface topology, conformational changes, and membrane-protein interactions.

Reference Publications:

1. "The Effect of Large Magnetic Fields and the g-factor Difference On the Triplet Population in Photosynthetic Reaction Centers", C.E.D. Chidsey, M.G. Roelofs and S.G. Boxer, *Chemical Physics Letters*, 74, 113 (1980).
2. "Picosecond Spectroscopy in Photosynthetic Models", R.R. Bucks, I. Fujita, T.L. Netzel and S.G. Boxer, in *Picosecond Phenomena II*, R. M. Hochstrasser, W. Kaiser and C.V. Shank, Eds., Springer-Verlag, Berlin, 1980, p. 322.
3. "Laser CIDNP Study of the Reaction Between Photoexcited Flavins and Tryptophan Derivatives at 360 MHz", E. F. McCord, R.R. Bucks and S.G. Boxer *Biochemistry*, 20, 2880 (1981).
4. "Solution Properties of Synthetic Chlorophyllide - and Bacteriophyllide - apomyoglobin Complexes", Karen A. Wright and Steven G. Boxer, *Biochemistry*, 20, in press (1981).

5. "Chlorophyll-Amino Acid Interactions in Synthetic Models", Steven G. Boxer and Rodney R. Bucks, Israel Journal of Chemistry (Special Photosynthesis Issue), in press (1981).
6. "UV Excimer Laser Photo-CIDNP of Amino Acids at 360 MHz", Elizabeth F. McCord and Steven G. Boxer, Biochimica Biophysica Research Communications, in press (1981).
7. "Oriented Properties of the Chlorophylls: Electronic Absorption Spectroscopy of Orthorhombic Pyrochlorophyllide a - Apomyoglobin Simple Crystals", Steven G. Boxer, Atsuo Kuki and Karen A. Wright, Proceedings of the National Academy of Sciences, USA, submitted.
8. "Psec Spectroscopic Studies of Models for the Primary Photochemistry of Photosynthesis", R.R. Bucks, I. Fujita, T.L. Netzel and S.G. Boxer, submitted to the Journal of Physical Chemistry.

8. INTRINSIC CHEMICAL REACTIVITY

John I. Brauman, Professor, Chemistry

Professional Associates:

F. K. Meyer

Graduate Students:

A. T. Barfknecht
P. S. Drzaic
R. L. Jackson*
J. M. Jasinski*
J. Marks

C. R. Moylan
M. J. Pellerite
C. M. Rynard
K. E. Salomon
W. Tumas

*Received Ph.D. during report
period

Agency Support:

NSF CHE 78-21064
PRF 10848-AC5,6

Technical Objective:

To obtain an understanding and separation of intrinsic (molecular) factors and solvation phenomena which affect the chemical reactivity and spectroscopy of ions and neutral molecules.

Approach:

We study a variety of chemical and photochemical reactions both ionic and molecular in both the gas and condensed phase. Comparison of results allows us to understand intrinsic effects (from the gas-phase) and intrinsic plus solvation effects (from condensed phases).

Research Report:

(1) Gas-Phase Ionic Reactions

Professional Associates: F. K. Meyer

Graduate Students: J. M. Jasinski M. J. Pellerite
C. R. Moylan W. Tumas

We have studied some sterically crowded acid-base reactions in order to look for unusual isotope effects, tunneling, and steric hindrance. We observe no quantum behavior (tunneling); we have determined directly the first kinetic isotope effect for a reaction of this kind. We have applied Marcus theory to an analysis of intrinsic barriers in displacement reactions. We have studied reactions of a novel species, the phenyl nitrene anion. We have reviewed the field of gas phase acidities of carbon acids.

(2) Electron Affinities, Photochemistry of Ions

Professional Associates: F. K. Meyer

Graduate Students: P. S. Drzaic M. J. Pellerite
R. L. Jackson C. M. Rynard
J. Marks

We have determined the electron affinities of a series of aliphatic mercaptide ions, which also gives new and more accurate bond strengths for the mercaptans. We have studied electron photodetachment from azide ions, determining the electron affinity of azide radical. We have studied HS^- producing an extremely accurate electron affinity for HS . We have reviewed the area of neutral thermochemistry obtained from electron affinities. We have continued an experimental and theoretical investigation of electronic states of negative ions which are best characterized as an electron bound to a molecular dipole. We have studied the gas phase photochemistry and spectroscopy of the unsaturated transition metal complex, iron tricarbonyl anion.

(3) Laser Induced Chemistry

Professional Associates: F. K. Meyer

Graduate Students: A. T. Barfknecht C. R. Moylan
P. S. Drzaic C. M. Rynard
J. M. Jasinski K. E. Salomon

We have continued our studies of infrared multiphoton chemistry. We have observed nonhomogeneous decompositions, suggesting a major flaw in most simple theories. We have used multiphoton infrared decomposition of ions as a probe for internal energy and obtained the first

experimental estimate of both collisional and radiative relaxation times for polyatomic ions.

Reference Publications:

- J. M. Jasinski and J. I. Brauman, "Rates of Proton Transfer between Pyridine Bases in the Gas Phase. Steric and Isotope Effects," J. Am. Chem. Soc. 102, 2906 (1980).
- B. K. Janousek, K. J. Reed, and J. I. Brauman, "Electron Photodetachment from Mercaptyl Anions (RS^-). Electron Affinities of Mercaptyl Radicals and the S-H Bond Strength in Mercaptans," J. Am. Chem. Soc. 102, 3125 (1980).
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- R. W. Wetmore, H. F. Schaefer III, P. C. Hiberty, and J. I. Brauman, "Dipole Supported States. A Very Low Lying Excited State of Acetaldehyde Enolate Anion," J. Am. Chem. Soc. 102, 5470 (1980).
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- M. J. Pellerite and J. I. Brauman, "Intrinsic Barriers in Nucleophilic Displacements," J. Am. Chem. Soc. 102, 5993 (1980).
- C. M. Rynard and J. I. Brauman, "The Photodissociation of Iron Tricarbonyl Anion," Inorg. Chem. 19, 3544 (1980).
- J. M. Jasinski and J. I. Brauman, "An Infrared Multiphoton Dissociation Study of Radiative and Collisional Relaxation of Vibrationally Excited CF_3O^- Ions," J. Chem. Phys. 73, 6191 (1980).
- M. J. Pellerite and J. I. Brauman, "Gas-Phase Ion-Molecule Reactions of Phenylnitrene Anion," J. Am. Chem. Soc. 102, 676 (1981).
- B. K. Janousek and J. I. Brauman, "Electron Photodetachment from HS^- . The Electron Affinity of HS^- ," Phys. Rev. A 23, 1673 (1981).
- R. L. Jackson, P. C. Hiberty, and J. I. Brauman, "Threshold Resonances in the Electron Photodetachment Spectrum of Acetaldehyde Enolate Anion. Evidence for a Low-Lying, Dipole-Supported State," J. Chem. Phys. 74, 3705 (1981).
- R. L. Jackson, M. J. Pellerite, and J. I. Brauman, "Photodetachment of the Azide Anion in the Gas Phase. Electron Affinity of the Azide Radical," J. Am. Chem. Soc. 103, 1802 (1981).

9. GEOCHEMICAL STUDIES OF AMORPHOUS AND CRYSTALLINE SILICATES,
SILICATE MELTS, AND AQUEOUS SOLUTIONS

Gordon E. Brown, Jr., Associate Professor, Geology

Professional Associates:

M. J. Apted, Research Associate, School of Earth Sciences
P. M. Fenn, U.C. Davis
G. A. Waychunas, Research Associate, CMR

Graduate Students:

H. Boek
A. Hessenbruch*
M. F. Hochella, Jr.
B. Goldstein
K. D. Keefer**
J. E. Shigley

*Completed M.S. during report period.

**Received Ph.D. during report period.

Agency Support:

NSF, Geochemistry Program
Stanford Energy Research Institute
Memorex
Standard Oil of California

Technical Objectives:

(1) To study the structure and physical properties of chemically homogeneous and phase separated silicate glasses and melts as functions of composition and temperature in order to formulate structure-property-composition relationships for geologically relevant silicate melts. (2) To study the complexing of base metal ions in hydrothermal solutions in order to understand the processes resulting in the concentration of base metals in ore deposits. (3) To investigate the melting phenomenon of silicate minerals at the structural level. (4) To investigate the paragenesis of various silicate and phosphate minerals, particularly those from granite pegmatites.

Approach:

The short-range and micro-structures of silicate glasses and melts are studied by a combination of methods including (1) X-ray radial distribution analysis; (2) small angle X-ray scattering; (3) X-ray emission, absorption, and photoelectron spectroscopy; and (4) viscosity measurements. The structure of metal complexes in aqueous solutions is studied by X-ray absorption edge and EXAFS spectroscopy. Crystal structure determination is carried out in the usual manner using precision X-ray intensity measurements. High temperature crystal structure studies involve the use of a high temperature (up to 1400°C) furnace mounted in a four-circle diffractometer. Our studies of mineral paragenesis involve field mapping, electron microprobe analysis, emission spectrographic analysis and X-ray diffraction.

Research Report:

(1) Structural Studies of Silicate Melts and Glasses

Graduate Students: M. F. Hochella, Jr.
K. D. Keefer

Professional Associate: G. A. Waychunas

Our primary efforts in this area during the past year included (1) experimental and theoretical studies of microstructure and liquid immiscibility in several silicate melt systems containing alkaline earth cations; (2) X-ray scattering studies of aluminosilicate melts and glasses in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ which were designed to investigate the variable structural role of aluminum and its effect on viscous flow in this system; (3) viscosity studies of melts and crystal-melt mixtures in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system; and (4) EXAFS studies of Ca-, Ti-, and Fe-bearing silicate glasses.

The study of melt immiscibility in the system $\text{KAlSi}_2\text{O}_6-\text{CaMgSi}_2\text{O}_6-\text{SiO}_2$ was carried out in order to determine the effect of metastable liquid immiscibility on crystal growth in this geologically simple system. The compositionally extensive metastable solvus was experimentally determined by observation of opalescence and small angle X-ray scattering in glasses which were quenched from the melt, subsequently heat-

treated, and, in certain cases, devitrified at one bar pressure. It was found that phase separation increased the rate of crystallization of the melt but did not induce internal nucleation of crystals. The greater basicity of the alkaline earths (Ca and Mg) relative to transition metals appears to be the reason that the solvus is completely metastable in this system but is stable in analogous transition metal-bearing systems.

Single-phase glasses of composition $25\text{CaO}-25\text{MgO}-50\text{SiO}_2$ and $26.9\text{CaO}-19.3\text{MgO}-53.8\text{SiO}_2$ were examined using small angle X-ray scattering and TEM methods for evidence of microstructure. The objective of this study was to gain a better understanding of the rapid crystallization of these melts. Although small crystals with diameters 1500\AA and above were detected in heat-treated glasses, no microstructure on the order of $30-1000\text{\AA}$ was revealed in this study. It was concluded that the rapid crystallization observed in these systems does not depend on the presence of a microstructure.

An alternative explanation for the above observations was found by examination of the polymeric structure of the melt. This effort led to the development of a theory based on a non-random equilibrium distribution of non-bridging oxygens among the silica tetrahedra in the melt. This approach is a significant departure from previous polymeric theories of silicate melts because it does not require differences in the degree of polymerization of the melt to explain differences in certain properties. Silica activity is described by the non-random nature of this distribution and the relative crystallization rates of melts are explained by differences in the concentration of silica monomers and dimers predicted by differences in SiO_2 activity. Phase separation is accounted for by the non-ideal mixing of tetrahedra with different numbers of bridging oxygens, particularly of tetrahedra with zero and four bridging oxygens. The relatively large concentration of monomers and dimers predicted in phase separated melts accounts for their rapid rate of crystallization.

Our X-ray scattering and viscosity studies of melts in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ have the objective of defining the structural role of

aluminum and relating this role to the dramatic variations in viscosity as Al_2O_3 is added to the $\text{Na}_2\text{O}-\text{SiO}_2$ system. X-ray radial distribution studies of glasses quenched from melts in this system provided no evidence of a mixture of IV- and VI-coordinated aluminum as has been suggested by several earlier workers. Our work is supported by the collaborative efforts of F. Gallener (Xerox Research Labs) and T. Soules (General Electric Research Labs) which involved laser Raman spectroscopy and molecular dynamics simulations, respectively, on melts and glasses from the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. Based on a synthesis of all available data, we have proposed a new type of polymeric unit of composition $\text{Al}_2\text{SiO}_{10}^{-10}$ which consists of three tetrahedra sharing a common oxygen. One of the major precedents for proposing this unit is its presence in mullite, $\text{Al}^{\text{VI}}[(\text{Al}_{1+2x}\text{Si}_{1-2x})^{\text{IV}}\text{O}_{5-x}]$, an important liquidus phase in the systems $\text{M}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ where $\text{M} = \text{Li}, \text{Na}, \text{K}$. The increasing concentration of this tricluster unit as Al_2O_3 exceeds Na_2O (SiO_2 constant) is consistent with the precipitous drop in viscosity and precludes the need to invoke aluminum octahedral units in the aluminum-rich regions of this system.

We have also carried out X-ray radial distribution studies of $\text{NaAlSi}_2\text{O}_6$ and $\text{NaAlSi}_3\text{O}_8$ composition glasses quenched from 10 and 15 k bars pressure, respectively. Our objective here was to examine the possibility of a pressure induced change in aluminum coordination from IV to VI as has been suggested recently by H. Waff (U. Oregon). Such a coordination change in natural melts may indeed occur in the Earth's upper mantle and result in significant changes in transport properties; however, we found no evidence for an aluminum coordination change in the two high pressure glasses studied.

The viscosity studies in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, begun during the last report period, have been completed. These data are consistent with the above mentioned structural studies of glasses quenched from these melts. A series of viscosity experiments were also conducted on a crystal-melt mixture in this system with the crystal to melt ratio increasing during the viscosity measurements. The observed seven order of magnitude increase in viscosity when this ratio reaches 0.25 is

consistent with observed viscosity changes measured during the crystallization of the Makaopuhi Lava Lake in Hawaii. The crystal-melt mixture examined in our study remained Newtonian up to a crystal/melt ratio of 0.25 and showed none of the thixotropic behavior observed in metallurgical slags.

The viscosities, short-range structures, and limits of liquid immiscibility in the system $\text{BaO-BaF}_2\text{-SiO}_2$ were examined with the aim of gaining a better understanding of and optimizing a silicon electrodeposition technique recently developed by Elwell, Feigelson and DeMattei of CMR. Viscosity measurements in this system proved to be impossible with our rotating cup viscometer. However, after analysis of available data, we have suggested the substitution of Ge or Al for Si in this system to enhance the density contrast between the silicon metal and the melt. Neither substituting element should significantly alter the short range melt structure, interfere with the electrodeposition process, or significantly affect the photovoltaic properties of silicon.

During the last several months of this report period, a number of EXAFS and X-ray absorption edge spectra were obtained on Ti- and Ca-bearing silicate glasses and several crystalline model compounds. The objectives of this work were to define the coordination geometry of Ca and Ti in silicate glasses and to determine the oxidation state of Ti. We found that the coordination number of Ca is commonly VII or VIII in silicate glasses and that the Ca coordination polyhedron is significantly more distorted in the glass (and melt) than in analogous crystalline compounds. These data are the first known to us which define the coordination geometry of Ca in silicate glasses and melts. Ti was found to be predominantly IV-coordinated and in both 3+ and 4+ oxidation states in the glasses examined.

During the report period we have purchased a Mossbauer spectrometer and a controlled oxygen fugacity furnace. These instruments are presently being installed and will be used in our study of the structural role of iron in silicate melts.

(2) Metal Complexes in Aqueous Solutions

Professional Associates: M. Apter
G.A. Waychunas

EXAFS and X-ray absorption edge spectra were obtained for several dozen aqueous solutions containing the base metals Fe and Zn and the halogen Cl and differing in ionic strength and pH. The objective of this study is to lay the groundwork for planned studies of the structure of base metal complexes in hydrothermal solutions at elevated temperatures and pressures. The overall aim of this work is to gain a better understanding of the way in which base metals such as Fe, Cu, and Zn are complexed during transport in hydrothermal solutions in the Earth's crust. Analysis of the iron chloride solution data is now relatively complete and shows that Fe is octahedrally coordinated by water molecules in all the Fe(II)-chloride solutions examined. We also found that Fe(II)-O bond distances decrease with increasing chloride/iron ratio, pH, and total FeCl_2 concentration. Slight intensification of the 1s \rightarrow 3d pre-edge peak with increasing FeCl_2 concentration suggests that chloride may be mixed with water as a nearest neighbor octahedral ligand. Our work on Fe^{3+} -chloride solutions showed that iron coordination changed from VI to IV as chloride concentration was increased from 7.8M to 15M in 1.0M FeCl_3 solutions. Hexa-aqua complexes were found to transform to tetra-chloro complexes as a function of chloride concentration.

A high temperature (up to 500°C)-high pressure (up to 1 k bar) cell has been completed recently and will be used to carryout EXAFS studies of solutions of similar and lower ionic strengths under PT conditions simulating those experienced by hydrothermal solutions in the Earth's crust.

(3) Structural Study of Crystalline Silicates

Professional Associate: P. M. Fenn
Graduate Student: H. Boek

During the report period, new structural data on olivines,

$M_2^{VI}Si_4$, where M = Mg, Fe, Mn, Co, Ni, Ca were combined with existing data to synthesize a critical review of this geologically important structure type. A general model was developed for explaining the variation of physical properties and crystal structure with composition, temperature, and pressure. The primary feature of this model, which accounts for the PTX stability of the olivine structure type, involves a limited dimensional mismatch between relatively rigid SiO_4 tetrahedra and relatively flexible MO_6 octahedra which share edges with the tetrahedra.

In a separate effort, we have obtained high temperature (up to 1000°C) structural data on an alkali feldspar of $K_{0.58}Na_{0.42}Si_3AlO_8$ composition and are presently collecting intensity data on a plagioclase feldspar of $Ca_{0.94}Na_{0.06}Al_{1.94}Si_{2.06}O_8(An_{94})$ composition. We have developed a new high temperature furnace for use on our four-circle diffractometer which will permit data collection up to 1200°C and plan to take data on the An_{94} crystal at a temperature as near the melting point (1550°C) as is possible with our furnace. Extrapolation of structural parameters, as a function of temperature, to the melting temperature for each of the structures provides some insight to the changes and possible limits to changes of certain bond lengths and angles. Following this procedure for the alkali feldspars, (K, Na) $AlSi_3O_8$, we have identified one alkali metal-oxygen band which appears to be limited in its thermal expansion and may be the key structural element in defining the upper thermal stability of the feldspar structure type. When similar high temperature data are available for the Ca-feldspar, a general model for the structural changes accompanying feldspar melting will be possible.

(4) Paragenesis of Silicate and Phosphate Minerals

Graduate Students: A. Hessenbruch
B. Goldstein
J. E. Shigley

We have completed a combined field-laboratory study of Ba-Ti mineralization in the New Idria District of San Benito County. This

work involved the characterization (chemical, optical, and structural) of thirty mineral species, including one unknown and possibly new Ba-Ti silicate species. The vein-filling assemblage of Ba-Ti silicates and associated Cu-sulfide minerals probably formed at a temperature of less than 70°C based on the presence of anilite ($\text{Cu}_{1.75}\text{S}$) which breaks down to other phases above this temperature.

Our study of phosphate paragenesis in granitic pegmatites is also nearing completion. Chemical and structural characterization of the phosphates and associated silicate phases is now completed and a model for the chemical alteration of the Mn- and Fe-bearing lithium phosphates has been developed. A series of melt-growth synthesis runs have been made during this report period in an attempt to grow lithiophilite, LiMnPO_4 , from the melt.

Another mineralogic study completed during this report period involves characterization of the clay mineralogy of the Butano and Whiskey Hill Formations in exposures along the San Andreas Fault near Stanford. The chlorite content of the Butano clay distinguishes it from the Whiskey Hill montmorillonite. The primary objective of this study was to devise a means of distinguishing between the two formations that abut along the San Andreas Fault.

Reference Publications:

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2. J. R. Clark and G. E. Brown, Jr., "The crystal structure of rasvumite, KFe_2S_3 ," *Amer. Mineral.* 65, 477-482 (1980).
3. G. E. Harlow and G. E. Brown, Jr., "Low albite: an X-ray and neutron diffraction study," *Amer. Mineral.* 65, 986-995 (1980).

4. G. E. Brown, Jr., "Crystal chemistry of the olivines and silicate spinels," in Review in Mineralogy (Ed. P. H. Ribbe), vol. 5, 275-381 (1980).
5. K. D. Keefer, M. F. Hochella, Jr., and B. H. W. S. de Jong, "The crystal structure of the magnesium hydroxysulfate hydrate $\text{MgSO}_4 \cdot 1/3 \text{Mg(OH)}_2 \cdot 1/3 \text{H}_2\text{O}$," Acta Crystallogr.
6. J. E. Shigley and G. E. Brown, Jr., "Phosphate mineralogy of the Stewart Pegmatite, Pala District, San Diego County, California," Prog. Geol. Soc. Amer. Ann. Mtg. 12, 521 (1980).
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10. PHOTOELECTRONIC PROPERTIES OF SOLIDS

R. H. Bube, Professor and Chairman, Materials Science and Engineering
Professor, Electrical Engineering

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A. Lopez-Otero
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Graduate Students:

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C. Eberspacher
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* Received MS during report period

** Received PhD during report period

Agency Support:

DE AT03 70047
SERI 8031
SERI 8087
SERI 9330
NSF 06574

Technical Objectives:

To investigate the photoelectronic properties of solids, both crystalline and non-crystalline, in order to understand the underlying phenomena and to improve the properties and performance of electronically active materials and devices, particularly those involved in the photovoltaic conversion of solar energy.

Approach:

To couple a materials synthesis and device fabrication program closely to develop an understanding of transport and junction properties for film-on-crystal and all-film heterojunctions, heteroface junctions and Schottky barriers, particularly in materials systems potentially suitable for large-area thin-film solar cells for terrestrial applications.

Research Report:

(1) Photoelectronic Properties of II-VI Heterojunctions

Graduate Students:	T. Anthony	F. A. Ponce
	J. Nielsen	J. Werthen
	K. Nishimura	

Research has had five principal areas of concentration: (1) preparation and properties of low-resistance ohmic contacts to p-type CdTe, (2) high-resolution transmission electron microscopy on CdTe, (3) correlation of surface properties of CdTe with Schottky barrier and junction properties subsequently formed, (4) chemical vapor deposition of large bandgap window materials on CdTe substrates, and (5) close-spaced vapor transport deposition of CdTe films.

A survey of metal contacts to p-type CdTe single crystals has revealed that the best contact is one prepared by vacuum deposition of CuAu onto a surface that has been etched with $K_2Cr_2O_7:H_2SO_4$. The contact resistivity on 0.5 ohm-cm p-type CdTe is between 0.1 and 0.5 ohm-cm². The contact resistivity increases if subjected to heat treatment, but is stable in air at room temperature apparently for periods of years. Contacts of CuAu and Cu on a chromate etched surface were compared in detail with similar contacts on a methanol-bromine etched surface through measurements of J-V curves vs T, photovoltaic response and Auger analysis. CuAu contacts on a chromate etched surface are describable in terms of a thermally assisted tunneling model with a barrier height of about 0.60 eV. Au contacts on either a chromate-etched or a methanol-bromine-etched surface can be described equally well by a thermally-assisted tunneling model or by a thermionic emission model; in either case, the barrier height is about 0.1 eV larger on the methanol-bromine etched surface than on the chromate etched surface. Auger analysis indicates that chromate etching produces a tellurium rich surface that plays a key role in determining subsequent contact properties.

The principal areas of advancement in high resolution transmission electron microscopy (HRTEM) include high resolution atomic imaging of CdTe, atomic motion at the edge of a CdTe crystal observed by HRTEM,

defect imaging in CdTe, and imaging of a TeO_2/CdTe interface. This latter work represents the first high resolution imaging of an interface with CdTe or of an interface between two compounds. The oxide is seen to be epitaxial with good coherence between crystallographic planes in spite of the large difference in lattice parameters. This is possible only because the TeO_2 layer is oriented with the $\langle 011 \rangle$ direction coincident with a $\langle 110 \rangle$ direction of the CdTe substrate. In addition the layer is rotated around the $\langle 011 \rangle$ direction so that one set of $\{111\}$ planes in the TeO_2 layer matches coherently with a set of $\{111\}$ planes in the CdTe. This match eliminates the existence of defects at the interface itself, which has a width of only about one atomic plane.

The effect of heat treatment in hydrogen on the surface of p-type CdTe crystals has been monitored by measurements of surface photovoltage. A correlation has been established between the amount of band bending on the surface and the open-circuit voltage found in a subsequently formed Schottky barrier. For minimum band bending, open-circuit voltages become increasingly large; such low amounts of band bending can be achieved by typical heat treatments in hydrogen at 350 to 400°C for 5 to 10 minutes. Values of open-circuit voltage in excess of 0.93 V have been observed in n-CdS/p-CdTe heterojunctions prepared on hydrogen heat-treated CdTe surfaces. Schottky barriers formed on heat-treated surfaces with such metals as Au, Cr, Sn, In and Y have shown open-circuit voltages in excess of 0.6 V, with an apparent correlation between metal workfunction and open-circuit voltage, the largest being observed for Y on a heat-treated surface. A freshly etched p-type CdTe surface is found to have 60 mV of band bending, an oxidized surface in air for 2 weeks has 150 mV, and a hydrogen annealed surface has 5 to 10 mV. These results suggest that hydrogen heat treatment acts to passivate interfacial states to produce more ideal surfaces for junction formation. Junctions formed on hydrogen-annealed surfaces have been stable for over 1½ years in a laboratory environment.

(2) Photovoltaic Heterodiodes Based on Indium Phosphide

Graduate Students: C. Eberspacher
C. C. Wong

A comprehensive investigation is being made of the surface properties of single crystal InP substrates and of the consequent effect on Schottky barriers and heterojunctions formed on these surfaces. Principal techniques being used include surface photovoltage and internal photoemission measurements.

Surface photovoltage measurements show that a decrease in band bending of the InP occurs with heat treatment in hydrogen between 400° and 450°C. Below 400°C no effect occurs, and above 450°C the band bending again increases. These results appear to be quite similar to those reported for CdTe in Section (1), and may correspond to removal of oxide by hydrogen heat-treatment at lower temperatures, and the generation of a non-stoichiometric InP surface for higher heat-treatment temperatures.

Internal photoemission measurements are being used to investigate the influence of etchant and oxidation environments compatible with heterojunction production by spray pyrolysis on InP, using Schottky barriers and MIS structures. A significant difference is found in plots of internal photoemission yield vs photon energy depending on the oxidation state of the surface. An interfacial oxide layer acts to preferentially attenuate low energy carriers photoexcited in the metal overlayer. A numerical integration of the simple Fowler form for photoemission modified for tunneling through an interfacial barrier has been used to calculate internal photoemission response curves in good agreement with experimentally measured values. This kind of approach promises to yield information on the interfacial barrier height and width relatively independent of minor defects often making I-V measurements difficult to interpret. Application of this theoretical model to the data requires also knowledge about the variation with photon energy of the proportion of the light energy actually absorbed in the metal layer; a careful analysis of the absorbed fraction of photon flux vs photon energy for gold films is being

carried out.

(3) Photoelectronic Properties of Zinc Phosphide Crystals, Films and Junctions

Graduate Students: C. Y. Ng
F. C. Wang

The electrical properties of Zn_3P_2 crystals grown by sublimation (physical vapor transport) and by iodine transport, as well as of large-grain polycrystalline material grown by sublimation, have been measured by conductivity and Hall effect measurements as a function of temperature. The II-V compound Zn_3P_2 appears to be a promising semiconductor for several applications, especially for large area solar cells, but only limited research has been carried out to date on its defect structure, common electrically-active imperfections, and other electrical properties.

In single crystals scattering is controlled by charged impurity scattering at low temperatures and acoustic lattice scattering at high temperatures, with a typical maximum mobility value of 10 to 20 $\text{cm}^2/\text{V}\cdot\text{sec}$. In polycrystalline samples the mobility is thermally activated with an activation energy of 0.072 eV at higher temperatures and 0.028 eV at lower temperatures, presumably due to intergrain potential barriers. A computer modelling of the Hall effect and conductivity data indicated acceptor levels with ionization energies of \approx 0.02, 0.25 and 0.47 eV for the sublimed crystals and polycrystals, and of 0.034 and 0.14 eV for crystals grown with iodine transport; densities for these levels were in the 10^{15} to 10^{16} cm^{-3} range, except for the 0.47 eV deep levels that appear to be present in much higher densities in all samples, of the order of $5 \times 10^{18} \text{ cm}^{-3}$.

Contacts to Zn_3P_2 are made with Ag, Au or a AuAg alloy, vacuum evaporated onto the Zn_3P_2 . All showed a linear I-V dependence, but in some samples the actual contact resistance increased appreciably at low temperatures as the bulk resistivity also increased. The hole density could be increased to $4 \times 10^{17} \text{ cm}^{-3}$ by diffusion doping with Ag acceptors. Vacuum heat treatment decreased the hole density by 10^3 ,

presumably by removing the interstitial phosphorus acceptors. Strong temperature-independent photoconductivity is observed in the vacuum annealed samples, corresponding to a majority carrier lifetime of about 3×10^{-6} sec.

Several single crystal samples were investigated by Auger profiling. The results indicate that Zn_3P_2 is readily oxidized to ZnO , but that a hydrogen heat treatment acts to prevent or minimize oxidation.

Thin films of Zn_3P_2 prepared by close-spaced vapor transport generally show an excess of Zn under electron microprobe analysis. A careful survey of the films themselves indicates that this excess Zn is concentrated at the surface of the films, and at voids and defects within the bulk of the film, the overall excess of Zn decreasing as surface layers of the film are removed. The use of a source consisting of $\text{Zn}_3\text{P}_2 + \text{InP}$ appeared to yield the most consistently stoichiometric film showing the highest electrical conductivity, although contamination with In could also be detected.

(4) Preparation and Properties of Evaporated CdTe Films Compared with Single Crystal CdTe

Graduate Students: C. Fortmann
T. Thorpe

A hot-wall vacuum evaporation system for deposition of CdTe films is proceeding through the design, construction and testing stages. While this apparatus preparation is in progress, CdTe homojunctions have been prepared by the hot-wall vacuum evaporation of n-type CdTe onto large grain polycrystalline CdTe substrates by Dr. Walter Huber (now a Post-Doctoral Fellow with us) working with Professor Adolfo Lopez-Otero at the Johannes Kepler University in Linz, Austria. The substrates were grown by the CMR Crystal Growth Laboratory at Stanford, who are also involved heavily in the single crystal portion of this program, as described below. Junctions were analyzed by J-V measurements, EBIC, spectral response of quantum efficiency, and theoretical model of the spectral response. EBIC measurements indicate minority carrier diffusion lengths of $L_n =$

1.8 μm for electrons in the bulk p-CdTe, and $L_p = 1.2 \mu\text{m}$ for holes in the n-type CdTe layer deposited by hot-wall vacuum evaporation. These values are in excellent agreement with values for L_p and L_n obtained by parameter fitting the spectral response: $L_p = 1.0 \mu\text{m}$ and $L_n = 1.5 \mu\text{m}$. Short-circuit currents were small in these cells because the n-type layer was 5 μm thick (optimum about 0.3 μm). Theoretical estimation of the optimal practically achievable efficiency was about 14%.

To date the CMR Crystal Growth Laboratory has grown over fifty single crystals of CdTe for various research activities of the group, the last four of which are the beginning of a special series to investigate crystal growth variations and doping effects. Use of crystal regrowth and vibration during growth both increase crystal quality. Higher electrical activity of phosphorus acceptors in CdTe is achieved when 0.1% excess Te is used in place of 0.5% excess Te (added to reduce pressure in the ampoule). The results obtained are in general agreement with the basic study of the CdTe:P system by Selim and Kröger.

Properties of grain boundaries in CdTe large-grain polycrystalline samples are also being investigated. The grain boundary resistance on three samples of n-type CdTe showed thermal activation energies of 0.17, 0.33 and 0.44 eV. Photoexcitation of the grain boundary produced a large decrease in this activation energy, with some effect being indicated for extrinsic photoexcitation as well as for intrinsic. In a sample of p-type CdTe a polycrystalline grain boundary had a thermal activation energy of 0.44 eV, but the resistance was almost totally independent of photoexcitation. Investigation of grain boundary properties and the possibility of grain boundary passivation will be continued.

(5) Heterostructures, Homojunctions and Schottky Barrier Solar Photovoltaic Convertors Based on CdTe Prepared by Hot-Wall Flash Evaporation

Graduate Student: M. S. Casey

Samples of thin film CdTe prepared by a hot-wall flash

vacuum evaporation technique at C.I.E.A. del I.P.N. in Mexico City have been received and analyzed in terms of their thickness, optical transmission, chemical composition, electrical conductivity, and surface morphology. Thermoelectric power measurements will be used to analyze transport in more conducting films. Films that show close to stoichiometric Cd/Te ratios tend to be high resistivity.

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11. NONLINEAR OPTICAL PROPERTIES AND APPLICATIONS OF SINGLE CRYSTAL
FIBER LiNbO_3

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Agency Support:

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AFOSR-F49620-81-C-0047	JSEP-ONR-632
ARO-DAAG29-81-K-0038	
NSF-CHE-791-12673	
NSG-2372	
DOE-LLL-3488009	

Technical Objective:

To grow single crystal fibers of LiNbO_3 and other transparent optical crystals and to study their optical and nonlinear optical properties.

Approach:

During the past year we completed construction of a single crystal fiber growth station. Growth of the 1 mm to less than 50 μm diameter fibers is accomplished by a laser heated pedestal growth technique. Using this apparatus based in the Stanford Materials Research Center, we have grown single crystal fibers of Nd:YAG, LiNbO_3 and Al_2O_3 .

We have investigated the domain properties of LiNbO_3 and have found that the single crystal sample of 150 μm in diameter and 2 cm in

length is composed of three intersecting domains. The crystals are single and are optically transparent. Light has been focussed into the fibers and is transmitted as expected.

Sapphire fibers have also been grown up to 20 cm in length at 150 μm diameter. They are mechanically strong and optically transparent. These fibers are useful for optical access to combustion zones where higher temperatures and pressures prevent the use of normal windows.

We plan to investigate nonlinear interactions in LiNbO_3 . This material should support electro-optic modulation, second harmonic generation and parametric oscillation. However, efficient nonlinear interactions require good control of crystal diameter. This has led to the design and construction of a new growth station for fiber pulling. The new station should be in operation in the Fall of 1981, under support of the new Single Crystal Fiber Thrust Program.

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3. R. L. Byer, "Frequency Conversion via Stimulated Raman Scattering," *Electro-Optical Systems Design* (February 1980).
4. K. Bennett and R. L. Byer, "Computer Controllable Wedged Plate Optical Variable Attenuator," *Applied Optics* 19, 2408 (15th July 1980).
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9. G. Giuliani, Y. K. Park and R. L. Byer, "Radial Birefringent Element and Its Application to Laser Resonator Design," paper R.21, Journ. Opt. Soc. Am. 70, 1410 (November 1980).
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11. R. L. Byer and M. D. Duncan, "A 100 usec, Reliable, 10 Hx Pulsed Supersonic Molecular Beam Source," Journ. Chem. Phys. 74(4), (February 1981).
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12. STUDIES IN CATALYSIS

J. P. Collman, Professor, Chemistry

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Agency Support:

NIH GM17880
NSF CHE78-09443
NSF CHE77-22722

Technical Objective:

The long-range goals of this research are to model metalloenzymes, to develop homogeneous, multi-metallic catalysts, and to invent electrode catalysts for multi-electron reductions.

Approach:

We are preparing transition metal porphyrin complexes which mimic the active sites in certain hemoproteins--hemoglobin, myoglobin, and the cytochrome P-450 oxygenase family. We are preparing binary, "face-to-face" porphyrins which are intended to serve as catalysts for the oxygen cathode in a fuel cell. We are also developing organo-transition metal reagents for stoichiometric organic synthesis and

exploring their reaction mechanisms.

Models for Myoglobin and Hemoglobin

We have continued to modify our capped porphyrins and measure competitive equilibrium binding of oxygen and carbon monoxide. Efforts to grow single crystals for X-ray diffraction are underway.

Models for Mixed-Function Oxygenase

We have completed the first stage of our work synthesizing analogue models for the ferrous form of cytochrome P-450. These porphyrins have internally delivered thiol and thiolate ligands as well as a "picket-fence".

Preparation of Catalytic Electrodes

We have discovered a more active catalyst for the 4-electron reduction of dioxygen in aqueous acid at a graphite electrode. We have further elucidated the stereochemical features of our basic catalyst. Work continues to improve the potential and durability of these catalysts, which may become useful in fuel cell technology.

Transition Metal Clusters and Fischer-Tropsch Catalysis

We have constructed a new cyclic and flow reactor for investigating the reaction between CO and H₂ in acidic molten salts catalyzed by transition metal clusters and heterogeneous particles. Mechanistic studies of this reaction are nearly complete.

Site-Isolated Homogeneous Catalysts

We have prepared a superior, silica-bonded, bidentate phosphine ligand as well as π -Cp silica-bonded ligands. Immobilized catalysts derived from these ligands are being studied in the context of the oxo reaction. These studies are directed towards understanding steps in the reaction mechanisms which might involve more than a single metal center.

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13. THEORETICAL PHYSICS OF COOPERATIVE PHENOMENA

S. Doniach, Professor, Applied Physics

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Agency Support:

NSF DMR79-13102 (I. Lindau, Principal Investigator)
NSF DMR80-07934
NSF-MRL through CMR

Research Reports:

(1) Motion of Vortices in Disordered Superconducting Films

Work with S. Trugman has been on a study of the motion of vortices injected into a superconducting film by means of an external magnetic field. We are interested in films of variable composition for which the chemical potential to inject a vortex is a random function of position. In the absence of drag the motion of vortices is normal to the gradient of the potential, so that the vortices move along contours of constant potential. Then, depending on their thermal energy, they will execute orbits which may either be closed around potential minima ("lakes") or about potential maxima ("islands"). At the intermediate energy there will always be open orbits which traverse the sample leading to finite dissipation of an imposed supercurrent. We show that the power spectrum of the thermal noise associated with a thermal population of injected vortices will go to zero as a power of the frequency, ω^{β} , where β is a

universal index derived in terms of the fractal character of the orbits. For a finite vortex mean free path resulting either from interaction with normal electrons or from vortex-vortex interactions, the system will have finite zero frequency resistivity.

(2) Melting of the Abrikosov Vortex Lattice in Layered Composites

Work with Claude Deutsch has considered the effects of interlayer coupling on melting of a lattice of vortices injected into a stack of superconducting films by an external magnetic field. We have applied a theory previously developed¹⁾ for a discussion of melting in smectic liquid crystals. In this picture the transverse London penetration depth $\lambda_L = \lambda / nd$, where λ is the bulk penetration depth, d the film thickness, and n the number of films in the stack, is considered to be still comparable with the sample size. The thermally induced unbinding of dislocation pairs in the vortex lattice is inhibited by the formation of lines of discommensuration ("strings"), changing the Kosterlitz-Thouless melting instability to a first order transition. The change in melting temperature is estimated in the limit that the film spacing becomes larger.

(3) Quantum Fluctuations in Superconducting Films

For granular metallic films, or 2-dimensional arrays of Josephson junctions, the tunnelling of Cooper pairs between the grains leads to a Coulomb charging energy $4e^2/c(n_{ij})^2$, where n_{ij} is the number of Cooper pairs and c the junction capacitance. For reasonably large grains (larger than the superconducting coherence length) n_{ij} may be treated as conjugate to the relative phase between the grains leading to a zero point motion of the superconducting phase which can, even at zero temperature, destroy the coherence of the superconductivity above a critical value of the ratio $4e^2/2cZJ$, where J is the Josephson coupling energy of a junction and Z is the number of nearest neighbors in the Josephson lattice. We show that for the 2-dimensional film the

nature of the zero temperature critical point is that of the λ -point of liquid ^4He in three dimensions (two space and one time) with $4e^2/c$ playing the role of temperature. The character of the frequency dependent precursor diamagnetism is studied in the vicinity of the quantum critical point.²⁾

(4) X-ray Spectroscopy of Mixed Valence Materials

Work with Se-Jung Oh has been on the calculation of photoelectron spectra from mixed valence materials. We consider an impurity atom, such as Ce, in a metallic host, using an Anderson model description of the mixed valent state. The effect of the removal of a core hole is to change the occupancy of the localized f-level in the mixed valence impurity. By means of a Green's function decoupling scheme we calculate the relative final-state probability of having 0, 1, or 2 electrons in the f-level of the atom with the core hole. Each of these final states will contribute a peak in the XPS, whose relative weights will in general be different from the relative occupancies of the various mixed valent states before the arrival of the x-ray.

(5) Polarization Dependence of X-ray Absorption by Atoms on Metallic Substrates

Work with D. Foley has been on a study of the dependence of the photoabsorption cross section on the direction of polarization of an x-ray impinging on a molecular cluster. We are using this to simulate the spectra of adsorbates on metallic surfaces such as sulfur on nickel. The surface of the Ni is simulated by a square of Ni atoms with a sulfur bound on one side. By use of a multiple scattering program developed in our group,³⁾ the angle dependence of the l-s photoabsorption edge of S (observed by J. Stohr of SSRL) may be calculated, and some conclusions reached about the geometry of the S-Ni binding site.

(6) Bosonisation of 2-band Hubbard Model

Work with Dana Browne has been on a 1-dimensional model of a system of fermions with short range Coulomb interactions moving in a two-band system where a narrow band overlaps a broad one. Models of this type are of interest in connection with mixed valence systems (though these are generally 3-dimensional) and organic conductors. By means of a representation of fermion operators in terms of charge and spin density operators, the instabilities of the interacting fermion system may be mapped onto instabilities of coupled classical Coulomb gasses in two dimensions (one space and one time).

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- 3) C. Natoli, D.K. Misemer, S. Doniach, and F.W. Kutzler, Phys. Rev. A 22, 1104 (1980).

14. THEORETICAL AND EXPERIMENTAL STUDIES IN BIOPHYSICS

S. Doniach, Professor, Applied Physics

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Agency Support:

NIH GM25217-03
NSF Biology

Research Report:

(1) Calculation of X-ray Absorption Edge Spectra

A program for use of multiple-scattered wave computations of photoabsorption cross sections applied to molecular clusters of biological interest is continuing.

Work on simple transition metal complexes has been published.¹⁾ Calculations of dependence of the cross section on the direction of the x-ray polarization relative to the molecular axes have been performed for the cluster $\text{Mo}(\text{O}_2\text{S}_2)$ and compare quite well with observations. The K-absorption edge is strongly polarization dependent, with edge features resembling those of molybdate (MoO_4) or thiomolybdate (MoS_4) when the \vec{E} -vector is oriented along the O_2 or S_2 axes respectively. The next stage is to attempt calculations on a model for the Cu binding site in plastocyanin for which single crystal absorption data has recently been obtained at SSRL.

Calculations for the L-edge spectrum of rare earth compounds (ErCl_4) have also been performed and compared with data for both the

anhydrous and hydrated crystal.²⁾ Calculations give a pronounced absorption peak at threshold (the "white line") in reasonable agreement with experiment. The calculations suggest that the intensity of this line is strongly dependent on the molecular environment created by the surrounding ligands (a molecular cage effect).

(2) Anomalous Small Angle Scattering Studies of Proteins and Membranes
Labelled with Tb³⁺

A small angle camera system with modified linear detector system has been constructed for use at SSRL.

Anomalous scattering from proteins in solution may be used to obtain information on distances between heavy atoms bound to the protein and on the heavy atom-protein-density distribution function.³⁾ Data on parvalbumin (a Ca-binding protein from carp-muscle) has been taken and shows an anomalous signal of order 10% of total scattered intensity. Excellent signal/noise was obtained (noise levels in the range of 1/5% of total signal) with a few hours of data collection. The data is currently being analyzed.

Anomalous scattering data from centrifuged vesicles containing acetylcholine receptor from electric fish batteries (Torpedo Californica) has been taken with reasonable signal/noise. Preliminary analysis suggests that Tb ions bind preferentially to the distal end of the receptor relative to the bilayer center. We are attempting to see if additional Tb-binding sites may be opened up by the action of agonists.

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15. COAL SLAG PHENOMENA IN OPEN CYCLE MHD GENERATORS

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Professional Associates:

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Graduate Students:

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*Received PhD during report period.

Agency Support:

EPRI RP468-1

Technical Objective:

The technical objective of this research program is to provide an understanding of the effect of coal slag deposits on the performance of magnetohydrodynamic (MHD) generators. These deposits are expected to influence the fluid mechanics, electrical performance, and materials selections for MHD generators.

Approach:

The program involves studies of the fluid mechanics of slag layers including the mechanism of deposition, the effect of slag droplets and mineral vapor on plasma conductivity, and the effect of slag layers on the electrical performance of MHD generators. A special effort is made to incorporate extensive diagnostics into the experimental program for direct measurement of as many parameters as possible. The laboratory program is accompanied by a modeling effort which is useful both in understanding the physical processes which occur and in extrapolating results to other conditions or to larger scale systems.

Research Report:

(1) Ash Droplet Size and Concentration

A two-wavelength laser transmissometer has been used to make in situ measurements of ash droplet size and concentration in a coal combustion plasma. Combustor parameters were varied to achieve various ash loadings, fuel/air equivalence ratios, flame temperatures and residence times. The measurements were performed utilizing both Illinois #6 and Montana Rosebud coals. Ash droplet mean diameters of 1.4 to 2.8 μm have been observed with Illinois #6 coal and mean diameters of 1.3 to 2.2 μm have been observed with Montana Rosebud coal. Ash droplet size appears to be a decreasing function of temperature and to be relatively independent of stoichiometry, residence time and ash loading.

(2) High Temperature Slagging Electrodes

A high-temperature (1700-1900°K) platinum alloy capped magnesia electrode was developed and successfully tested for diffuse operation at current densities up to 3 amps/cm^2 . The transition current density for arcing was determined as a function of electrode temperature. The electrical characteristics (including electrode voltage drops) of a high-temperature electrode section and a cold electrode section were measured at three levels of magnetic field and compared. Hall voltage and interelectrode AC resistance distributions were measured and correlated with the plasma core behavior inferred from voltage probe measurements. A diffuse mode, two-dimensional model for current density and potential distributions was developed which includes the effects of slag layer hydrodynamics, slag layer energy transport, and assumed plasma boundary layers. Numerical solutions for this model are presented as a function of wall temperature and magnetic field.

Publications:

1. P. C. Ariessohn, S. A. Self, and R. H. Eustis, "Two Wavelength Laser Transmissometer for Measurements of the Mean Size and Concentration of Coal Ash Droplets in Combustion Flows," Applied Optics, August 1980.
2. Peter Carl Ariessohn, "Optical Diagnostic Measurements of Coal Slag Parameters in Combustion MHD Systems," High Temperature Gasdynamics Laboratory Report No. 119, August 1980. [Ph.D. Thesis].
3. Ron Michael Nelson, "Electrical Effects of Slag in a Diffuse Mode Magnetohydrodynamic Generator," June 1981. [Ph.D. Thesis].

16. EXPERIMENTS AT LIQUID HELIUM TEMPERATURES ON MACROSCOPIC QUANTUM EFFECTS,
MATERIAL PROPERTIES, GENERAL RELATIVITY, AND SUPERCONDUCTING ACCELERATORS

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C. W. F. Everitt, Adjunct Professor
B. Cabrera, Assistant Professor of Physics
H. A. Schwettman, Professor of Physics

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G. Kaiser	M. A. Taber
J. A. Lipa	R. C. Taber
P. F. Michelson	J. P. Turneaure

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S. Benjamin**	J. D. Phillips
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*Received PhD during report period.

**Received MS during report period.

Agency Support:

NSF PHY76-23559	NASA NAG2-62
NSF PHY80-14184	NASA NGR-05-020-019
NSF PHY76-80105	JPL 955057
NSF PHY76-80168	ERDA EY-76-S-03-0326, PA48
ARMY DASC60-77-C-0083	ERDA EY-76-S-03-0326, PA49
AFOSR 80-0067	
AFOSR 80-0026	
AFOSR F49620-78-C-0088	

Technical Objective:

This research is directed toward the study of the basic problems of physics using low temperature techniques. In addition to experiments studying the special properties of superconductors and helium for their sake, we exploit their unique properties to perform experiments in other fields of physics such as gravitation and relativity, biophysics and medicine, particle accelerators and the search for fractionally charged particles.

Research Report:

(1) Positron Source and Photon Counting Detector

Research Associates: J. M. Madey

Graduate Student: G. A. Westenskow

A source of magnetic ground state positrons at energies below 10^{-7} eV is required for operation of the positron free fall experiment. Positrons in this energy range cannot be obtained from natural β^+ emitters.

The approach we have adopted is to capture a small number of relatively low energy (~ 100 eV) positrons and to trap them within a solenoidal magnetic field between electrostatic mirrors. Provided that the trap proves to be stable, the positrons can readily be thermalized to energies of the order of 10^{-4} eV. Adiabatic expansion can be used to lower the energy to the required 10^{-7} eV.

The availability of low energy ground state electrons from a thermalization process of this type makes possible the development of a photo-electric effect detector for use at millimeter wavelengths. The detector is based on excitation of the $n = 1$ cyclotron level of magnetic ground state electrons trapped in a high Q cavity resonant at the cyclotron frequency. Theoretical estimates of the performance predict a noise temperature less than 1°K and quantum efficiencies of the order of 10%. Such a detector would have immediate application in millimeter wave radio astronomy.

We are now testing a prototype thermalizer which can function as a photon counting detector. Trapping and partial thermalization have been achieved; improvements in progress should help realize complete thermalization.

(2) Force of Gravity on Elementary Charged Particles and Surface Shielding Effect

Graduate Student: J. Henderson

Low energy electron beam techniques have been developed which permit the measurement of the force of gravity on single electrons and positrons, thus allowing a direct test of the gravitational equivalence of matter and anti-matter. The electron experiment has already been performed, yielding results which seem clear, but which also seem to indicate the presence of an unexplained shielding effect in the metallic drift tubes used in this experiment. Work has been directed toward exploring the nature of this shielding effect and the conditions under which it exists. There appears to be strong evidence for the presence of a large temperature dependence in the magnitude of the shielding. Experiments are now in progress to determine the detailed behavior of this temperature dependence.

Current efforts have concentrated on developing an electron/positron thermalizer. When completed, a higher ultra-low energy electron/positron flux will be possible, resulting in better experimental statistics. The positron measurements will provide considerable information on the electric fields associated with the shielding. Work is also being done to measure the lifetime of a He^+ ion in a strong magnetic field.

Other techniques are now being employed to study the surface properties of oxidized copper in an effort to understand the physical basis for the surface shielding effect. These techniques include microwave surface impedance studies, sensitive contact potential measurements with a vibrating plane capacitor, and high resolution magnetic susceptibility measurements.

(3) Search for Fractional Charge on Matter

Graduate Student: Jim Phillips

The purpose of this experiment is to search for fractionally charged particles (quarks) on superconducting niobium spheres supported by a magnetic field. The experiment measures the net electric charge on a niobium ball of mass approximately 10^{-4} gm. Fractionally charged particles, if they are contained on a niobium ball, would be observable as a non-integral net charge on the ball. Measurements have been made on 45 niobium balls with a sensitivity of approximately $\pm 0.02 e$, where e is the electron charge. The central issue in this experiment is to determine unambiguously whether or not the observed force is due to fractional charge or is caused by spurious dipole forces. The spurious forces have been accounted for and the results indicate that there are fractional charges on matter. Forty-five measurements have been made on sixteen balls, with nine results of $+1/3 e$, six of $-1/3 e$, and the rest of $0 e$. Out of the twenty-nine repeat measurements, sixteen have given no fractional charge change, and thirteen have given a change of magnitude $1/3 e$.

(4) Development of a Sensitive Cryogenic Gravitational Wave Detector

Research Associates: M. S. McAshan E. Mapoles
R. C. Taber P. F. Michelson

Graduate Student: M. Bassan

Using cryogenic techniques it is possible to make extremely sensitive gravitational radiation detectors. We have developed a low temperature detector which, in its present configuration, is more than 10^3 times more sensitive than the room temperature antennas which have been used until now. The main concept of the detector is a 4800 kg aluminum antenna which will be maintained at a temperature between 1.5 and 4 K. The amplitude of vibration in the fundamental mode of the antenna is converted to an electrical signal by a superconducting resonant transducer, and amplified by a Josephson effect parametric device operating at 9 GHz. During the past year various components were finally tested, and assembly of the detector completed. A preliminary test of the cryostat without the antenna was successful, and the complete detector

was cooled to liquid helium temperature for the first time. Preliminary measurements show that the detector is capable of a noise temperature for pulse detection of 3 mK. Potential for at least another order of magnitude in sensitivity exists without substantial modification of the detector or cryostat.

In the next year we intend to use the detector in measurements of the background flux of gravitational radiation at a sensitivity level between three and four orders of magnitude better than previous experiments. The level of sensitivity attained will be sufficient to detect the radiation of less than $10^{-2} M_{\odot} c^2$ into gravitational waves of bandwidth 10^3 Hz at the galactic center. We also plan to pursue vigorously a program to improve the sensitivity of the detector with particular emphasis on the transducer.

(5) Interfacial Surface Energy Between Superfluid Helium-3A & B Phases

Graduate Student: B. J. Neuhauser

I will measure the surface energy between the superfluid A & B phases of helium-3 by observing the motion of the AB phase boundary when it encounters a grid while the helium-3 sample is being slowly cooled. A pickup coil senses the flux produced by magnetization of the superfluid phases and couples it into a SQUID via a superconducting transformer. Because $X_A > X_B$, changes in the distribution of A & B phases cause changes in flux which are readily detected by the SQUID system.

Cooling to millidegree temperatures is accomplished by demagnetizing a CMN salt pill which is in intimate contact with the helium-3. Thermometry is done by measuring the susceptibility of lanthanum-diluted CMN. Precise temperature and pressure control systems have been developed for this experiment.

(6) Experiments in Very Low Magnetic Fields

Research Associate: B. Cabrera

We have obtained magnetic fields smaller than 10^{-8} gauss in a cylindrical superconducting lead shield that is four inches in diameter and thirty inches long. This magnetic field level, an order of magnitude smaller than we had previously obtained, corresponds to at most a few flux quanta trapped in the superconducting shield. We are using a superconducting double point-contact magnetometer with a resolution of 10^{-9} gauss to measure the very small magnetic fields. We have constructed an apparatus to measure the magnetic flux trapped in a superconducting cylinder 1/2 inch in diameter by 4 inches long. We have the sensitivity to see individual flux quanta penetrating the walls of this cylinder, and thus study the pinning of flux in superconductors. One of these shields has been used in conjunction with a detection coil coupled to a SQUID as a magnetic monopole detector. Our present sensitivity is 1/50 of a Dirac monopole. Our data to date is consistent with zero magnetic charge.

(7) Nuclear Polarization of He^3

Graduate Student: M. A. Taber

We have used He^3 optical pumping techniques to produce dilute polarized He^3 and He^4 gas mixtures. Such mixtures have been successfully condensed into a low magnetic field region and the precession of the He^3 magnetization has been observed in an applied transverse field of 10^{-4} gauss by use of a SQUID magnetometer. Initial magnetization has been greater than 10^{-5} gauss with a signal to noise of 1000 to 1. We have completed a series of experiments to measure the spin-lattice relaxation time (T_1) of the liquid He^4 -polarized He^3 mixture under various conditions and as a function of applied field. The relaxation times vary from approximately 4 hours at 55 μ gauss to 35 hours at 1.8 mgauss for a bare Pyrex sample bulb. Using a solid H_2 wall coating of ~40 molecular layers thick has yielded a relaxation time of 130 hours at 2.9 mgauss. At lower fields the relaxation times approached those of the bare bulb.

These experiments are a continuation of an effort devoted to development of a He^3 nuclear gyroscope.

(8) Magnetocardiology (Joint Project with Stanford Hospital)

Graduate Student: M. C. Leifer

We are developing two new magnetic techniques for non-invasive clinical observation of human cardiac function. The first measures magnetic susceptibility changes associated with the motion of blood within the heart. The second technique involves the use of a superconducting gradient magnetometer to measure the magnetocardiogram, the magnetic field generated by the electrical activity of the heart. We have built a large magnetic shield and a computer signal-processing system. The clinical value of the magnetic field measurements will be determined by studying normal patients and patients with various cardiac diseases.

(9) Equivalence Principle Accelerometer

Adjunct Professor: C. W. F. Everitt

Research Associate: P. W. Worden, Jr.

The experiment is intended to test the application of cryogenic technology to a measurement of the uniqueness of free fall, particularly with regard to investigating the ultimate limitations to sensitivity and a possible earth-orbiting equivalence principle experiment. A pair of superconducting test masses of different materials are suspended in essentially frictionless linear magnetic bearings. The masses are cylindrical with dimensions optimized to minimize gravity gradient effects, and are free to move along the cylinder axis. An electronic control mechanism keeps each mass centered with respect to the casing by tilting the support plane provided by the magnetic bearing. The control efforts required to keep the masses centered are appropriately scaled and subtracted to one part in 10^5 , providing a signal proportional to any differential acceleration which may exist. The difference signal may then be recorded and Fourier analyzed to determine the relative amplitudes of the various frequency components.

The limiting sensitivity of the experiment on earth is set by seismic noise and the accuracy of the subtraction process. A difference of one part in 10^{12} in the ratio of inertial to gravitational mass is estimated to be the limit of sensitivity on earth. In low earth orbit the sensitivity is limited by tidal sloshing of the liquid helium refrigerant and is probably one part in 10^{17} .

(10) Relativity Gyroscope Experiment

Adjunct Professor: C. W. F. Everitt
Senior Research J. A. Lipa
Associates: B. Cabrera
J. T. Anderson
Research Associate: G. M. Keiser

In 1960 Professor Leonard Schiff of Stanford University suggested a new test of general relativity based on observing the precessions of very accurate gyroscopes in an earth-orbiting satellite. Since 1962, a group of physicists and engineers from the Hansen Laboratories and the Department of Aeronautics and Astronautics have been designing and developing the experiment using cryogenic techniques. A model of the flight gyroscope and liquid helium dewar has now been operating at Stanford for a number of years. The experiment is expected to be flown in 1985.

(11) Superconducting Meson Channel

Professor: H. A. Schwettman
Research Associate: R. C. Taber

A superconducting pion channel has been developed and constructed. It consists of two 10 ft. diameter torroidal superconducting magnets, each having 60 pancake forms. Cooling is achieved by conduction from liquid helium tubing placed on the edge of the coil forms. This novel application of large scale superconducting technology results in a large solid angle exceeding 1 steradian for the collection of pions. The purpose of the magnet is to collect and deliver pions for use in cancer therapy in a proposed hospital facility.

The present research program is devoted primarily to dosimetry and radiobiology measurements. These measurements are intended to provide the basis for designing and operating the proposed facility.

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17. EXCITED STATE DYNAMICS AND PHONON EFFECTS IN MOLECULAR PHASES

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Research Report:

- A. Laser-Induced Phonon Spectroscopy. Optical Generation of Ultrasonic Waves and Investigation of Electronic Excited-State Interactions in solids¹

Crossed laser pulse excitation generates high amplitude, counterpropagating, ultrasonic waves (acoustic phonons of selected wave vector) via direct coupling between the optical field and the material acoustic field. The technique allows optical generation of ultrasonic waves, conveniently tunable to at least 20 GHz. The coupling mechanism, which does not involve optical absorption, is discussed in detail in terms of electrostriction. The periodic density changes resulting from the acoustic waves cause spectral shifts whose magnitudes reflect the strengths of excited-state intermolecular interactions and excited-state phonon interactions. The first quantitative measurements of spectral shifts by laser-induced phonon spectroscopy (LIPS) are reported. In pentacene in p-terphenyl, spectral shifts on the order of 1 cm^{-1} are measured using laser-induced phonons propagating along the b crystallographic axis. Orientation of the phonon wave vector along various

crystalline directions allows investigation of the anisotropic excited-state intermolecular interactions.

B. Delocalized Electronic Excitations of Pentacene Dimers In A p-Terphenyl Host: Picosecond Photon Echo Experiments²

Photon echo experiments are performed on delocalized electronic excitations of optical dimer states. The delocalized dimer states are found to have very long coherence times; close to the coherent limit. The dimer dephasing is qualitatively similar to dephasing of pentacene monomers.

C. Electronic Excited State Energy Transfer, Trapping by Dimers and Fluorescence Quenching in Concentrated Dye Solutions: Picosecond Transient Grating Experiments³

Picosecond transient grating experiments are used to examine electronic excited state dynamics in concentrated dye solutions. A model based on radiationless excited state transport and trapping by dimers describes the phenomena responsible for fluorescence quenching. The trapping rate constant is found to have a cubic concentration dependence. Rhodamine 6G dimer lifetimes in glycerol and ethanol are 830 psec and < 50 psec, respectively. The difference arises due to the viscosity dependence of the dimer radiationless relaxation rate.

D. Electronic Excited State Transport in Random Systems: Time Resolved Fluorescence Depolarization Measurements⁴

Electronic excited state transport in a system composed of randomly distributed molecules, i.e., Rhodamine 6G in glycerol, is experimentally investigated. Time resolved fluorescence depolarization measurements which use a fluorescence mixing technique to give subnanosecond time resolution, provide a stringent test for theoretical work

on this subject. The results yield an R_0 value of 50 Å for R6G and confirm the results of the recent diagrammatic self consistent theoretical method. Mean-square-displacements and their time derivatives are reported. Energy transport is nondiffusive in the samples studied.

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18. CRYSTAL SYNTHESIS

R. S. Feigelson, Director, Crystal Synthesis, Center for Materials Research, Adjunct Professor, Department of Materials Science and Engineering
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Agency Support:

DOE through CMR	Quanta-Ray through CMR
NAVAIR through CMR	Lehigh University through CMR
NASA through CMR	JSEP (Auld)
ONR through CMR	ARCO (Shaw)
SERI (Bube)	

Technical Objective:

The Crystal Synthesis activity has two principal goals: (1) to generate a more detailed understanding of crystal growth and materials preparation processes, and (2) to produce a wide variety of materials with closely controlled properties for basic research and device applications.

Research Report:

(1) Electrodeposition of Silicon for Solar Cells

D. Elwell, R. C. De Mattei, R. S. Feigelson, R. A. Huggins,
and G. M. Rao

Silicon is the material most likely to meet the challenge of low production cost which is the most difficult requirement for terrestrial solar cells. The aim of this investigation is to develop techniques for the economic production of polycrystalline silicon by electrocrystallization from molten salts.

Inclusion-free deposits of silicon have been made on silver and graphite substrates at 750°C using a solution of K_2SiF_6 in the LiF/NaF/KF eutectic. The highest purity layers contain only 10 ppm of total impurities. This process therefore shows great promise for the production of large area solar cells. The material is p-type, with grain size typically 100-250 μ m.

An alternative approach which is being pursued is to deposit bulk silicon by a method analogous to the Hall process for aluminum production. This method relies on electrodeposition of silicon above its melting point, so that very rapid deposition rates can be achieved. A furnace has been designed and constructed for electrodeposition at temperatures in the range 1420-1500°C and the electrodeposition of silicon in the liquid state was achieved using a $BaO/SiO_2/BaF_2$ melt. The deposit is in the form of roughly spherical particles up to 1.5 gm in weight and 99.98% purity without any pre-electrolysis stage to enhance purification. Studies are in hand to improve the purity and to develop a process for efficient removal of the silicon from the melt.

(2) Growth of Single Crystal Optical Fibers

B. A. Auld, R. L. Byer, R. S. Feigelson, W. L. Kway, and
H. J. Shaw

An extensive single-crystal fiber research program was started recently to (1) develop equipment and techniques for the growth of single crystal fibers, (2) to study the growth and properties of fibers of various optical, dielectric, ferroic, laser, and structural materials which may be useful in device research, and (3) to investigate growth

mechanisms involved in fiber growth and fully characterize the properties of these fibers.

A pedestal growth apparatus has been designed and constructed for single crystal fiber growth similar to the modified float zone method. A CO_2 laser heat source is employed with a special differential pulling system which permits the pulling of fibers from a molten zone at rates in the range of 1-100 mm/min. Since small fiber diameters (25-200 μm) and steep temperature gradients are involved, the maximum allowable growth rates for these fibers are much higher than for bulk crystals of the same composition.

To date the emphasis has been on the growth of optical waveguiding single crystal fibers. Fibers of LiNbO_3 , $\text{Cd}_2(\text{MoO}_4)_3$, Nd:YAG, Al_2O_3 , and CaSc_2O_4 have been successfully grown in the 50-200 μm diameter range. Because of the extremely small diameters and the very long aspect ratio of these fibers, with lengths exceeding 10 cm in some cases; vibrations, ambient air turbulence, and laser power source stability are critical factors which limit the diameter uniformity. Fiber diameter monitoring, microprocessing, and feedback techniques are currently being developed to improve diameter control and make possible the growth of fibers in even smaller diameters which is necessary for single mode optical waveguiding. The growth of multiphase fibers from eutectic melts is planned in the near future.

(3) Piezoelectric Polymers

R. S. Feigelson, R. C. De Mattei, and R. K. Route

Polyvinylidene fluoride (PVF_2) polymer films have recently been shown to possess piezoelectric and pyroelectric properties comparable to ceramic materials and consequently have potential application as acoustic detectors/generators and as pyroelectric detectors. Its low acoustic Q, mechanical flexibility, and ability to withstand electric field strengths exceeding 30 V/ μm without depoling make it ideally suited for a number of sonic and ultrasonic applications where the ceramic materials are not particularly appropriate.

Currently there are only a few suppliers of PVF_2 material worldwide, and the selection of "piezofilm" is severely limited. One of the

long range goals of the PVF₂ program was to produce optimized PVF₂ polymer films through a close interaction with several device groups. The PVF₂ polymer film fabrication effort is being carried out at CMR using a melt casting technique. The process variables involved include melt casting, stretching, annealing, electroding, and poling. Beginning with the bulk polymer resin, a carefully controlled processing procedure is now being used to produce 10 μ m PVF₂ films having 30-50% greater piezoelectric activity than the best commercial material available.

The key factor affecting the electrical properties of PVF₂ films is their microstructure, which is influenced by the processing parameters. The main thrust of the Polymer Program is two-fold: an in-depth understanding of how processing parameters affect crystallinity and microstructure, and how in turn crystallinity and microstructure ultimately affect the bulk electrical properties. Detailed microstructural characterization using primarily x-ray diffraction techniques is currently being carried out after every processing step in order to accomplish this.

At the same time, the program is being broadened to include the study of other types of PVF₂ structures. These include the development of PVF₂ fibers in which a very high degree of crystallite orientation can be achieved, and the development of macroscopic blends and composites in which PVF₂ interacts mechanically with another polymer or a solid material such as a light-guiding optical fiber.

(4) Growth of Infrared Crystals for Acousto-Optic and Electro-Optic Applications

R. S. Feigelson, R. J. Raymakers, and R. K. Route

Over the last decade our laboratory has had a strong interest in the growth and characterization of a wide variety of ternary semiconductor compounds. By their nature these materials tend to be infrared (IR) transmitting and consequently find application in a wide range of IR optical applications such as mixers, modulators, and tunable fibers. During the past several years our main emphasis has been in two areas: (1) the prediction, growth, and characterization of new semiconductor compounds for IR applications; and (2) the development of new and improved techniques for the growth of the compound semiconductors.

In the area of prediction, by starting with known materials and considering factors such as the index of refraction, IR transparency, and low acoustic velocities, all of which affect the relative figures of merit, it is possible to generate potentially more active analogs by substitution of iso-electronic elements. Going one step further, having identified a potentially interesting candidate one can search for other compounds which may exist in the ternary system. Two classes of materials which hold considerable promise are the thallium sulfosalt chalcogenides represented by Ti_3AsSe_3 and the chalcopyrites such as AgGaSe_2 and CdGeAs_2 . (These three materials have previously been grown at CMR in high quality, single crystal form.) Using the approach of looking first for iso-electronic analogs and then for related ternary compounds, two totally unknown IR transmitting compounds were discovered and grown as single crystals: Ti_9BiTe_6 and AgTlSe .

AgGaS_2 is a good example of a compound semiconductor for which we are currently studying improved growth techniques. This material has extreme promise as an IR transmitting nonlinear optical material. It is most difficult to obtain in high optical quality, however, for several reasons: the material does not solidify congruently at the stoichiometric composition and the as-grown material contains finely dispersed precipitates due to apparent retrograde solubility. Furthermore, it expands along the optic axis during cooling which makes it very difficult to grow in sealed quartz ampoules without experiencing extensive cracking. Current growth technology utilizes a technique with postgrowth heat treatment in an Ag-S atmosphere to remove the precipitates. The yield from this procedure is relatively low and improvements in our understanding of the phase equilibrium in the Ag-Ga-S system are currently being sought.

(5) Growth of Urea Crystals

R. L. Byer, R. S. Feigelson, R. J. Raymakers, and R. K. Route

It has recently been shown by a number of investigators that crystals of urea have great potential for nonlinear optical applications, in particular, ultraviolet generation.

A program was started recently to develop both melt and solution growth techniques for the preparation of large urea single crystal

samples of high optical quality. Melt decomposition makes crystal growth from molten urea difficult and optical quality is poor. It is hoped that a technique for stabilizing urea melts can be developed which will permit growth by the Bridgman-Stockbarger or zone leveling method of crystal growth.

The growth of urea crystals from methanol, methanol-water, and other alcohol-based solutions has been demonstrated to the point of producing seed crystals. However, urea is exceedingly sensitive to changes in both composition and temperature stability, and autonucleation and veiling are persistent problems in typical aqueous growth systems. We are currently developing a hermetically sealed system with state-of-the-art precision in temperature control in order to provide a more stable growth environment.

(6) Growth of CdTe Crystals

R. S. Feigelson and R. J. Raymakers

Cadmium telluride crystals have been grown over the past few years for use as substrates for heterojunction photovoltaic cells. Boules are grown by the vertical Bridgman method in sealed quartz ampoules and until recently were typically polycrystalline with the number of grains per boule varying from three to twenty. Attempts to correlate polycrystallinity with various growth conditions such as growth rate, temperature gradient and composition did not yield useful information. Decanting experiments did show that the growth interface shape was concave with respect to the crystal, a condition which favors multigrain structures. It was found difficult experimentally to create a planar or slightly convex interface shape which would aid in minimizing this problem.

A few studies, particularly in the Russian literature, suggested that the introduction of low frequency acoustic vibrations into the growth system was beneficial with respect to increasing grain size.

A modification of our CdTe growth apparatus was made to permit the application of mechanical vibrations to the growth ampoule. The application of mechanical vibrations to the growth ampoule during growth produced dramatic results. Boules grown this way were mostly single, with many fewer grains than those produced previously. Etch pit densities

were significantly lower than crystals grown without vibrations. The exact mechanism or mechanisms responsible for the dramatic improvement in crystal quality is not understood. It has been demonstrated in our laboratory that vibrations in this frequency range can accelerate mixing. The effectiveness depends on the frequency and amplitude of the acoustic signal, the aspect ratio of the system and the fluid properties. Vibrations can also influence the temperature at the interface producing periodic growth and remelting which might influence crystal quality. Future work is centering on identifying the mechanisms involved in improved crystal quality, characterizing these crystals, and optimizing the process.

(7) Electrodeposition of Silicon Carbide

D. Elwell, R. S. Feigelson, and M. M. Simkins

Silicon carbide is widely used as an abrasive and is potentially of great importance as a high-temperature semiconductor. No method presently available has given reproducibly bulk crystals of semiconductor quality, and this is the first attempt to use electrodeposition for this purpose.

The best electrodeposition method for synthesizing SiC has been using a melt of composition $(1-x)\text{Li}_2\text{CO}_3; x\text{SiO}_2$ with $0.15 \geq x \geq 0.20$ at $1025 \pm 25^\circ\text{C}$, and with an applied potential of $0.45 \pm .05\text{V}$ versus SiC. Epitaxial deposits have apparently been achieved on α -SiC substrates but the substrates often delaminate in the molten salt bath. The most promising application of SiC electrodeposition is for electrowinning of granular material for abrasive powders, or as a coating technique.

(7) Stability of Crystal Growth from the Melt

K. S. Ahn, R. A. Carranza, D. Elwell, R. S. Feigelson, and W. A. Tiller

The problem of stability of growth of a plane interface is one of the most important in crystal growth. The aim of this investigation is to obtain a comprehensive set of data on maximum stable growth rates and material parameters in a model system, for comparison with theories of morphological stability.

Cesium cadmium chloride CsCdCl_3 has been chosen as the material for this investigation and has been found particularly suitable for direct observational studies at temperatures below 600-650°C where the thermal radiation is not troublesome. Cobalt has been found to be the most suitable dopant and a laser absorption method has been developed to study the Co-profile in the solid and liquid regions during growth.

The study includes Co segregation measurements using crystals grown by the Czochralski method. The equilibrium segregation coefficient for growth in the (0001) direction has been found to be 0.16 and segregation measurements in various crystallographic directions as a function of growth rate and crystal rotation rate have been made for comparison with a new theory of segregation.

(8) Growth of $\text{GdDy}_2(\text{MoO}_4)_3$ Single Crystals

B. A. Auld, R. S. Feigelson, and W. L. Kway

The rare earth molybdates $\text{Gd}_2(\text{MoO}_4)_3$ and $\text{GdDy}(\text{MoO}_4)_3$ belong to a class of materials recently found to be of great importance. These materials exhibit not only ferroelectric and piezoelectric properties, but also ferroelastic properties. When these materials are used in electro-optic or acousto-optic devices, the ferroelastic properties can be utilized to modulate electromagnetic or acoustic energy through the movement of domain walls when an electric field is properly applied.

The choice of $\text{Gd}_2(\text{MoO}_4)_3$ and $\text{GdDy}(\text{MoO}_4)_3$ for the present study was based on two factors: (1) great device potential, and (2) relative ease of single crystal growth. As indicated by previous studies, single crystals may be grown with reasonable success by the Czochralski technique. However, since second phase inclusions are an inherent problem with these material, together with the problem of the volatility of MoO_3 , further study and development of material preparation techniques is required in order to improve the compositional quality. Also, since there are several phase transitions which occur during cooling the crystals from the growth temperature, special techniques for annealing and quenching these crystals must be developed in order to obtain crack-free boules of reasonable size.

Single crystal fibers of $\text{Gd}_2(\text{MoO}_4)_3$ have recently been grown and are being characterized. Future work in this area will be in eliminating the growth defects and growing longer fibers.

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19. MACROMOLECULAR RESEARCH

P. J. Flory, J. G. Jackson-C. J. Wood Emeritus Professor of Chemistry

Professional Associates:

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B. Erman
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*Left during report period

Agency Support:

AFOSR 77-3293-A,B,C,D
NSF DMR 80-06624- A02

Technical Objective:

To develop a better basis for understanding macromolecules and for interpreting their properties and behavior.

Approach:

Currently investigations are under way in the following areas:

1. Theory of rubber elasticity. Relationship of stress to strain for diverse large deformations. Relationship to network structure and topology.
2. Statistical mechanics of stiff-chain molecules.
3. Liquid crystals: theory and experiment.
4. Investigations on the optical anisotropies of polymers and oligomers, including polystyrene, polyacrylates, polycarbonates, and poly (methyl methacrylate).
5. Electric birefringence of oligomers and polymers.
6. Theory of interphases of chain molecules in semicrystalline polymers, in monolayers and in membrane bilayers.

Reference Publications:

1. P. J. Flory, "Introductory Lecture: Levels of Order in Amorphous Polymers," Faraday Discuss. Chem. Soc., 68, 14 (1979).
2. D. Y. Yoon and P. J. Flory, "Molecular Morphology in Semicrystalline Polymers," Faraday Discuss. Chem. Soc., 68, 288 (1979).

3. J. P. Hummel and P. J. Flory, "Structural Geometry and Torsional Potentials in p-Phenylene Polyamides and Polyesters," *Macromolecules*, 13, 479 (1980).
4. B. Erman, P. J. Flory, and J. P. Hummel, "Moments of the End-to-End Vectors for p-Phenylene Polyamides and Polyesters," *Macromolecules*, 13, 484 (1980).
5. K. A. Dill and P. J. Flory, "Interphases of Chain Molecules: Monolayers and Lipid Bilayer Membranes," *Proc. Natl. Acad. Sci. USA*, 77, No. 6, 3115 (1980).
6. B. Erman, W. Wagner, and P. J. Flory, "Elastic Modulus and Degree of Cross-Linking of Poly(ethyl acrylate) Networks," *Macromolecules*, 13, 1554 (1980).
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20. PHOTOPHYSICS OF POLYMERS IN SOLUTION: ENERGY TRANSFER AND INTRA-MOLECULAR ROTATIONAL DIFFUSION

Curtis W. Frank, Associate Professor Chemical Engineering

Graduate Student:

P. D. Fitzgibbon (Received PhD during report period.)

Agency Support:

Petroleum Research Fund of the American Chemical Society
PRF 11105 AC 67

Technical Objective:

The objective of this research is to develop a model for electronic energy migration in aromatic vinyl polymers which are free to undergo intramolecular rotational diffusion.

Approach:

A major element of the photophysical behavior of the aromatic vinyl polymers is the formation of excimers, which are electronically excited states formed between coplanar aromatic rings, one of which is in a singlet excited state, the second in the ground state. There are two possible means by which excitation energy may be localized at such a geometrical structure. In the first, referred to as migrational sampling, absorption of radiation by a pendent aromatic ring is followed by a random hopping of the singlet exciton until competitive trapping occurs at an excimer forming site. Although the population of suitable excimer forming polymer chain conformations is small due to the steric repulsive forces in the opposed aromatic rings, the exciton trapping efficiency at a preformed excimer site is quite high. In addition, the remainder of the polymer chain acts as an "antenna" composed of many isolated aromatic rings each of which is capable of becoming excited and subsequently transferring the excitation energy along the chain by a non-radiative process. Thus, the overall sensitivity to

energy transfer is quite high. Finally, the excimer is an intrinsic trap as opposed to an extrinsic trap such as an added dopant which makes it possible to detect coupling between exciton hopping and chain vibrational modes, if such coupling exists.

In the second sampling mechanism, termed rotational sampling, the residence time of the excitation on any given aromatic ring is long with respect to the time required for Brownian rotational motion around backbone bonds. Thus, it is possible that the appropriate excimer forming geometry between aromatic rings on adjacent repeat units could be reached within the residence time. Since interconversion of excimer and non-excimer dyads involves short chain segmental motion around backbone bonds, excimer fluorescence is the ideal tool to study the contribution of internal potential energy barriers and bulk solvent viscosity to rotational diffusion processes.

Research Report:

In the first study (1), excimer fluorescence was used as a probe of the bulk viscosity dependence of intramolecular segmental motion in dilute solutions of poly(2-vinylnaphthalene) (P2VN) of number average molecular weight 300,000 and the dimer model compound, 1,3-bis(2-naphthyl) propane ($\beta\beta$ DNP). The viscosity of the toluene solvent was varied from 0.5 to 4.5 centipoise through application of hydrostatic pressures up to 450 megaPascals. The fluorescence behavior was analyzed in terms of Birks scheme I kinetics for the photophysics and Kramers theory for the segmental motion. The $\beta\beta$ DNP data were fit satisfactorily by the Kramers treatment in the intermediate friction regime. The P2VN results, on the other hand, were fit better by the high friction limit of the Kramers treatment, assuming that the effective local viscosity was different from the bulk solvent viscosity.

The second area of research involved the development of an analytical model for the molecular weight dependence of excimer formation in aromatic vinyl polymers in dilute solution (2). A one-dimensional random walk approach was shown to fit the experimental data for good solvents in which the polymer chains are extended. It is expected that the model will be inappropriate for poor solvents or high concentrations where

exciton hopping can occur across loops of the same chain or between different chains.

Reference Publications:

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2. P. D. Fitzgibbon, "Excimer Fluorescence as a Probe of Energy Migration and Segmental Diffusion in Polymers," Ph.D. Thesis, Stanford, 1980.

21. METAL FATIGUE STUDIES WITH DISCRIMINATING SPECIMENS

Henry O. Fuchs, Professor Emeritus, Mechanical Engineering
A.K. Miller, Associate Professor, Materials Science & Engineering
Drew V. Nelson, Assistant Professor, Mechanical Engineering

Graduate Students:

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*Received Ph.D. during report period.

Support:

Electric Power Research Institute

Approach:

We have used discriminating specimens to investigate complex multi-axial fatigue and the effect of mean stress on uni-axial fatigue. The location of failure on such specimens tells which of several hypotheses is more valid than the others for a given type of loading and a given specimen.

For both problems (multi-axial and mean stress effect) there are a multitude of contradictory theories or rules in current use. For multi-axial fatigue our specimens are designed so that they fail in region A or region B or C depending on the predictive power of theories X, Y, or Z. For the mean stress effect each of our specimens tells whether the effect is greater or less or equal to that predicted by any of the theories for the particular conditions of that specimen.

Research Report:

- A. We have shown that the fatigue damage done by 90 degree out of phase torsion and bending is greater than predicted by currently accepted theories based on shear stress.

Garud has developed a very promising theory based on plastic work.

- B. A given mean stress M usually changes the stress range R which corresponds to a given fatigue life and probability of failure from R_o to $R_o + \Delta R_m$. Our experiments seem to show that the relation between ΔR_m and M cannot be as simple as postulated by the currently accepted theories of Sines, of Morrow, of Smith-Topper-Watson, and of the coming revision of MIL.HDBK 5.

Publications:

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4. Lee, S.B., "Evaluation of Theories on Multiaxial Fatigue with Discriminating Specimens," Dissertation, Stanford June 1980.

22. CONFORMATION OF ADSORBED POLYMER MOLECULES SUBJECTED TO FLOW

G.G. Fuller, Assistant Professor, Chemical Engineering

Graduate Student:

Jen Jiang Lee

Agency Support:

NSF-CPE-8105497

Engineering Foundation RC-A-80-1E

Stanford Institute for Energy Studies

Technical Objective:

This research will focus on determining the extent of deformation and orientation of adsorbed polymer films by hydrodynamic forces. Particular emphasis will be placed on systems of importance in the adhesion of protective polymer coatings.

Approach:

Ellipsometry shall be used to measure polymer film thickness and surface coverage directly in a flowing system. The design and sensitivity of the apparatus should allow the detection of flow-induced changes in film thickness, surface coverage and optical anisotropy.

Research Report:

An ellipsometer designed to measure the properties of thin, polymer films subjected to flow has been constructed and initial measurements are in progress. The system under study consists of a wide range of molecular weight samples of polystyrene dissolved in toluene with chrome used as the adsorbent. The flow cell has been designed in order to induce velocity gradients up to 10^4 sec^{-1} . The experiments are being complemented by modelling studies at the molecular level from which the distortion and alignment of attached polymer chains by hydrodynamic forces can be predicted.

Reference Publications:

1. G. G. Fuller, "Dynamics of an Adsorbed Polymer Molecule Subjected to Flow," Symposium on Adhesion Aspects of Polymeric Coatings at the 159th Meeting of the Electrochemical Society, May 10-15, 1981, Minneapolis, Minn.

23. ION IMPLANTATION AND LASER ANNEALING OF SEMICONDUCTORS

J. F. Gibbons, Professor, Electrical Engineering

Graduate Students:

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K. L. Conway**
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report period.

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report period.

Agency Support:

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ARPA MDA 903-80-C-0238
ARPA MDA 903-78-C-0128
ARPA MDA 903-78-C-0290
AROD DAAG 29-78-G-0119
AROD DAAG 29-81-K-0061
NSF DMR 78-19970

Technical Objective:

The general objective of the research performed in this group is to study the physics of ion implantation and beam annealing processes in semiconductors. Efforts during this past year have been directed toward improvements in the predictions of range distributions in ion implanted targets and the development of laser and electron beam techniques for annealing implantation-produced damage in ion-implanted materials and recrystallizing polysilicon films.

Research Report:

(1) Range and Damage Distributions in Ion Implantation

Graduate Student: L. A. Christel

The objective of this project is to investigate recoil and damage effects which occur during ion implantation in multilayered targets.

Discussion of results

(a) A computer program which simulates the ion implantation process and is based on the numerical integration of coupled transport

equations has been used to calculate a number of quantities of interest. Oxygen recoil range distributions which result when ions are implanted into silicon which is coated with a thin layer of oxide have been calculated and agree well with available experimental SIMS data. Simple empirical relations have been found which approximate these distributions with exponential functions for general ion energy and oxide thickness. The recoil yield of silver which results when 255 keV krypton is implanted through thin films of silver has been experimentally investigated using Rutherford backscattering techniques. Experimental results are again in good agreement with the theoretical calculations, the yield reaching a maximum of about 5 for a silver thickness of about 400 Å.

(b) Another area investigated is the stoichiometric disturbance which occurs in ion-implanted compound semiconductors. It is found that when compound semiconductors are implanted, there exists a region near the surface where the concentration of the heavier element of the compound exceeds that of the lighter element, whereas at deeper depths the lighter element is in excess. The effect is greatest for heavy ions and in those compounds in which the elements differ widely in mass (e.g., Se implanted in InP).

(c) Finally, the production of amorphous silicon has been investigated in terms of the number of lattice atoms which are displaced during implantation. The results of calculations, when compared to experimental data, indicate that displacement of about 10% of the crystalline lattice results in amorphous silicon.

Reference publications:

- [1] L. A. Christel, J. F. Gibbons and S. Mylroie, "An Application of the Boltzmann Transport Equation to Ion Range and Damage Distributions in Multilayered Targets," J. Appl. Phys. 51 (12), 6176, (1980).
- [2] L. A. Christel, J. F. Gibbons, and S. Mylroie, "Recoil Range Distributions in Multilayered Targets," Proceedings of the Second Int. Conference on Ion Beam Modification of Materials, Albany, N.Y. July 1980 in Nvc. Inst. Methods, Summer 1981.

- [3] L.A. Christel and J.F. Gibbons, "Silver Recoil Yield Resulting From Krypton Implantation, J. Appl. Phys. (to be published July 1981).
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(2) Annealing of $Hg_{1-x}CdTe$

Graduate Student: K. L. Conway

Objective: To study laser and/or thermal annealing of $Hg_{1-x}CdTe$ for eventual use in p-n junction fabrication.

Results: Rutherford backscattering (RBS) and channeling have been investigated as a means of studying layer regrowth and sample quality for $Hg_{1-x}Cd_xTe$. RBS spectra of bulk $Hg_{1-x}Cd_xTe$ were obtained and machine parameters adjusted to permit resolution of the Hg, Cd and Te signals. Channeling measurements were made on several samples. The best minimum yield obtained was 10% as compared to 4% for Si. While indicating poor crystal quality, this yield is sufficiently low to enable channeling to be used to study layer regrowth.

Work has been started on possible use of an encapsulant to contain Hg in the sample during an anneal. Currently CdTe is being tested as an encapsulant.

Work has been started on thermal annealing. A literature search has been made for materials parameters needed for laser annealing calculations.

(3) Recrystallization of Polycrystalline Silicon by a Scanned CW Beam

Graduate Student: Kwing Lee

Objective: To study the recrystallization of polycrystalline silicon films by means of a cw laser and other energy beam sources, with emphasis on device applications.

Results: Previous results have been included in past reports. During the last year, the effect of power level on the recrystallization process was presented [1]. The melt and regrowth of a polycrystalline silicon layer directly deposited on a single-crystal silicon substrate,

as induced by a cw argon laser, was studied [2]. Lateral epitaxy, which is the extension of such a regrown layer from a single-crystal seed area laterally to an area where the polycrystalline silicon lies on top of a dielectric layer of silicon dioxide was also studied [3]. As an alternative to the laser, a cw xenon arc lamp, which is more energy efficient and has a larger beam size than a laser, was used to recrystallize polycrystalline silicon deposited on quartz [4]. In addition, previous results comparing the resistivity reduction in heavily doped polycrystalline silicon using cw laser and pulsed lasers were accepted for publication [5].

Reference publications:

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- [3] T. I. Kamins, T. R. Cass, C. J. Dell'Oca, K. I. Lee, R. F. W. Pease, and J. F. Gibbons, "Lateral Epitaxial Recrystallization of Deposited Silicon Films on Silicon Dioxide," J. of Electrochemical Society 128, 1151 (1981).
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- [5] T. Shibata, K. F. Lee, J. F. Gibbons, T. J. Magee, J. Peng and J. D. Hong, "Resistivity Reduction in Heavily Doped Polycrystalline Silicon Using CW Laser and Pulsed Laser Annealing," J. Appl. Phys. (to be published).

(4) Laser Annealing and Laser Assisted Diffusion in GaAs

Graduate Student: Wes I. Nissim

Objective: To study laser annealing and laser assisted diffusion in GaAs.

Results: Gallium arsenide is a promising potential candidate for laser processing since conventional thermal treatments are not yet fully satisfactory. The annealing of ion implanted GaAs using laser techniques has been investigated and some mechanisms that enhance the recovery of the lattice and the activation of the dopants have been identified. Then as a substitute to ion implantation, cw laser irradiation was used to diffuse dopants in GaAs from surface sources to create thin n^+ layers. These diffused layers were optimized to form nonalloyed ohmic contacts that were successfully utilized in the fabrication of different GaAs metal semiconductor field effect transistors.

GaAs is a brittle material that decomposes at low temperature. Decomposition (As evaporation) limits the amount of heat that can be transferred to the substrate with a cw laser. Temperature calculations have shown that a beam with an elliptical shape produces a more gradually distributed temperature gradient than a circular beam. It has also been observed that above the threshold of laser induced damage on GaAs, the surface of the wafer decomposes to form the oxide $\beta\text{-Ga}_2\text{O}_3$. Using an elliptical beam, this oxide has been grown continuously by overlapping laser scans with the sample in either laboratory air or an oxygen environment. The heat transferred to the substrate during the growth has allowed the annealing of low dose, deep implanted layers.

Another mechanism that could produce annealing at low substrate temperatures is the epitaxial recrystallization of ion implanted amorphous layers in the solid phase regime. Complete regrowth in GaAs has been obtained after a thermal anneal at 475°C for 10 min. Some limiting factors to the regrowth have been identified. This process has the potential to enhance cw laser annealing of GaAs at incident laser powers that would leave the substrate free from damage.

As a substitute for ion implantation a technique to introduce dopant into GaAs without damaging the substrate has been developed. The source consists of a spin-on $\text{SiO}_2/\text{SiO}_2$ film. Tin atoms are diffused

into the substrate on active sites by a combination of thermal and laser treatments. A variety of procedures have been studied to explore the possibilities of this technique. Thin n^+ layers on semi-insulating GaAs substrates have been obtained in this way. Direct evaporation of metal (Ti-Pt-Au) permits the formation of ohmic contacts of low specific contact resistance ($R_{SC} \leq 10^{-6} \Omega\text{-cm}^2$). These nonalloyed contacts are found to be thermally stable (up to 400°C) in contrast to conventional Au-Ge contacts. The mechanism of low resistance contact formation is believed to be a result of the combination of heavy doping and interface reaction between the source and the substrate. This new contact technology has then been optimized and applied in the fabrication of different GaAs MESFET structures where the same metal was used for both the ohmic contacts and the Schottky barrier.

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- [6] Y. I. Nissim and J. F. Gibbons, "CW Laser Annealing of Low Dose Implants in GaAs" in *Proceedings of 1980 Materials Research*

24. MÖSSBAUER EFFECT AND RELATED PHENOMENA

S. S. Hanna, Professor, Physics
N. S. Dixon, Assistant Professor, Physics

Professional Associates:

D. Ramsay

Graduate Student:

L. S. Fritz

Agency Support

NSF PHYS 77 24631

Our research is directed toward combining the fields of nuclear physics and low temperature physics in order to study both fundamental and applied physics phenomena. Many of our studies are done at low temperatures (in a ^3He - ^4He dilution refrigerator) and provide information which cannot be obtained with conventional NMR or NQR techniques.

Research Report:

(1) Mössbauer Effect Studies of Electronic Relaxation in Thulium Alloys

Graduate Student: L. S. Fritz

The effect of electronic relaxation on Mössbauer Effect (ME) spectra of rare earth materials has been of interest for several years. Most of the work in this field has involved Kramers' ions Yb, Dy, and Er. This work deals with the non-Kramers' ion ^{169}Tm . Three alloys, TmCu , $\text{Tm}_{0.85}\text{Y}_{0.15}\text{Cu}$ and $\text{Tm}_{0.70}\text{Y}_{0.30}\text{Cu}$ were studied. These materials all order magnetically at temperatures near 10K. Thus, ME spectra were taken over the temperature range from 65 mK to 15 K in a ^3He - ^4He dilution refrigerator. The ME spectrometer is mounted horizontally and runs

with source velocities up to 80 cm/sec.

The ordering temperatures and splittings between the Mössbauer lines observed in the spectra at the lowest temperatures, together with crystal field parameters obtained elsewhere for the isostructural compound ErCu, allow a determination of crystal field parameters and magnetic exchange fields for the three Tm alloys. These in turn lead to the wave functions and energies of the 13 crystal field states which are necessary for an electronic relaxation analysis of the higher temperature ME spectra.

There are two basic types of electronic relaxation which need to be considered, spin-spin and spin-lattice relaxation. Spin-spin relaxation involves interactions between the spin of the Tm ion of interest with either the spins of other Tm ions or with the spins of the conduction electrons. Spin-lattice relaxation involves the absorption and/or emission of one or more lattice phonons. In the relaxation analysis, one defines a relaxation matrix, the elements of which depend on the type of relaxation one is dealing with.

The calculation of the matrix elements for the two types of relaxation comprises a major part of the present work. Also, the temperature dependence of the relaxation rate turns out to be very different for the two types of relaxation. Thus, by studying the relaxation rate as a function of temperature, one can differentiate between the two types. This work has shown that spin-spin relaxation is dominant below ~5 K while spin-lattice relaxation is dominant above ~5 K for all three alloys.

25. PSEUDOPOTENTIAL METHODS IN PHYSICS

W. A. Harrison, Professor of Applied Physics

Professional Associate:

S.-Y. Ren

Graduate Students:

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P. A. Stevens
J. M. Wills

*Received PhD during report period.

Agency Support:

NSF DMR 80-22365
ONR N00014-79-C-0072
NSF-MRL through CMR

Technical Objectives:

To understand the electronic structure of solids and its relation to the properties of the solid.

Research Report:

Our recent development of tight-binding theories of covalent and ionic solids allowed analytic calculations of total energies, except for interatomic repulsions which either required lengthy computer calculation or empirical interactions. This year we attempted to approximate the full numerical approaches to the repulsion sufficiently to carry them out analytically; this was basically seeking the asymptotic formula for large distances and assuming that it remained approximately valid at interesting distances. The method was directly successful for closed-shell systems. It was found that the excess electronic kinetic energy of the p-states (of energy $\epsilon_p = -\hbar^2 \mu^2 / 2m$) dominated the repulsion and the asymptotic form for the interatomic interaction

$$V_0(d) = \eta_0 \frac{\hbar^2 \mu^2}{2m} \mu d e^{-(5/3)\mu d}$$

was very accurate over several decades of V_0 and to small enough values of d to be applicable to the solid. The value of the coefficient $\eta_0 = 71$ depended upon a normalization of the states as if the asymptotic form of the wavefunction was valid for all r and much more accurate results could be obtained by adjusting η_0 to one of four values, depending upon the quantum number of the valence p-state of the anion; then they gave good predictions for the equilibrium spacing, cohesion and bulk modulus for divalent and trivalent, as well as monovalent, AB compounds. This analysis also suggested a formulation of the total energy without Madelung energies; this provided an alternative to the traditional Born theory of ionic crystals which is of comparable accuracy but very much simpler. A similar method was found applicable for covalent solids with a correction factor for the η_0 coefficient which was predicted theoretically to be $2^{2/3}$. It eliminated the major portion of the error of the earlier computational theory but did not provide as accurate predictions as were those for the ionic solids.

We also made a study of the interatomic interactions in simple metals, finding that the use of Fermi-Thomas theory with rigorous pseudopotential theory gives extremely simple, and purely repulsive interactions. The balancing volume-dependent attractive term dominates the cohesion, but has little effect on the detailed configuration-dependent interactions which determine the elastic constants, vibrational spectra, etc. This fits well with a recent finding by J. Chelikowsky that the simple metals are well describable by Fermi-Thomas theory though the atoms are not; then the cohesion of the metal becomes understandable entirely in terms of the deviations from the Fermi-Thomas theory of the free atom. We are in the midst of this analysis of the simple-metal theory.

Finally we have combined a peripheral-state theory by S. G. Louie with our tight-binding theory of nonmetals to correct the principle defect in our earlier description of the electronic band structure. This enabled us to obtain improved tight-binding parameters, considerably better bands, a bond-orbital theory with the same covalent and polar energies entering bonding and dielectric properties, and the possibility

of systematic corrections to the bond-orbital approximation, without significantly complicating the calculation of solid-state properties.

Reference Publications:

1. W. A. Harrison, "Fifty Years of Metals Theory," in Felix Bloch and Twentieth Century Physics, (eds.) M. Chodorow, R. Hofstadter, H.E. Rorschach, and A.L. Schawlow (Rice University, Houston, 1980).
2. Shang-Yuan Ren and W. A. Harrison, "Semiconductor Properties Based Upon Universal LCAO Parameters," Phys. Rev. B 23, 762 (1981).
3. Shang-Yuan Ren, "Extended Bond Orbital Theory of Piezoelectric and Transverse Charges," Phys. Rev. B 22, 2908 (1980).
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8. W. A. Harrison, Review of "Electrons at the Fermi Surface," (ed.) M. Springford. Nature 290, 347 (1981).
9. W. A. Harrison, "Total Energies in the Tight Binding Theory," Phys. Rev. B, in press.
10. W. A. Harrison, "New Tight-Binding Parameters for Covalent Solids Obtained Using Louie Peripheral States," submitted for publication.
11. W. A. Harrison and J. Wills, "Interatomic Interactions in Simple Metals," to be published.
12. W. A. Harrison, "Electronic Structure of Nonmetals under Pressure," to be published.

26. HIGH-RESOLUTION AND IN-SITU INVESTIGATIONS OF SMALL PARTICLES AND REACTIONS ON SURFACES

K. Heinemann, Adjunct Professor, Materials Science and Engineering

Professional Associates:

H. Poppa	L. Larson
R. Anton	E. Kong
M. Prutton	

Graduate Students:

K. W. Carey
M. Avalos-Borja
K. Shia Yu

Agency Support:

NASA - NCC 2-30
NASA - NCA 2-OR-745-901
NSF - 77-05958
NASA - NCC 2-46
NASA - NCC 2-103

Technical Objective:

Increase the understanding of fundamental aspects in thin film growth and catalysis.

Approach:

(a) Characterize nanometer-size metal particles, deposited on substrates, by sophisticated methods of high-resolution transmission electron microscopy and computer analysis.

(b) Determine the growth behavior of small metal particles during physical and chemical vapor deposition by in-situ transmission electron microscopy studies under controlled conditions (uhv and deposition parameters).

(c) Investigate the reaction of deposit small metal particles with gases under controlled vacuum and temperature conditions, using the in-situ transmission electron microscopy approach.

Research Report:

(1) Weak-Beam Dark-Field Image Interpretation

Graduate Student: M. Avalos-Borja

The use of computers as aid for TEM image interpretation has increased considerably during the recent years. In particular, the interpretation of weak-beam dark field (WBDF) equal thickness fringes for the determination of the habit of nonometer-size crystallites has been emphasized to be dependent on the concomitant ability of image intensity calculations using the many-beam dynamical theory (DT). On the other hand, some researchers have been using simple 2-beam kinematical theory (KT) calculations for similar image interpretations. No attempt has been reported to quantify the necessity and the limitations of either approach. We have conducted comparative DT and KT calculations, emphasizing the definition of the number and selection criterion of the beams that should be included in DT calculations which are intended to be superior in accuracy to KT calculations.

We modified a program developed by Yacamán, following the n-beam dynamical theory principles, to accept up to 100 beams at various selection criteria, and studied the influence of the number and selection criterion of the beams included in the calculation on the extinction distance and its dependence on the crystal thickness. The beams were selected according to the following criteria: (A) closest distance from the Laue circle; (B) highest values of $((h^2 + k^2 + l^2) * s_g)^{-1}$; (C) highest values of $((h^2 + k^2 + l^2)^{1/2} * s_g)^{-1}$; (D) highest values of $((h^2 + k^2 + l^2) * s_g^{1/2})^{-1}$; and (E) closest distance from the transmitted beam. (s_g is the excitation error). The resulting extinction distance was determined as average over 5 or 18 Pendellösung fringes. The extinction distance calculated with the 2-beam KT was used as a reference. It was found that all cases, with the exception of criterion A, converge to a common value (which is slightly below that predicted by the KT). The sequence D behaves most steady and converges fastest, and we determined this selection criterion with at least 40 beams to be the most accurate combination.

The results further indicate that the DT calculations yield a thickness dependence of the fringe spacings. However, these variations

are usually well within 5% of the respective values calculated with the 2-beam KT, and errors stemming from not using enough beams or using an improper beam selection criterion can be greater than the improvement of accuracy experienced by turning from simple 2-beam KT calculations to complicated multi-beam dynamical theory computations.

Additional useful information can, in principle, be expected from n-beam DT calculations with respect to (a) the intensity of the fringes and (b) the spacings between any two individual fringes. The fringe intensity variations, clearly found for certain conditions in the n-beam DT calculation results, are extremely difficult to experimentally reproduce. This was found to be due to the strong dependence of this effect on the direction of the tilt axis, the control of which is often not possible. The spacings between any two individual fringes lack systematic consistency and are believed to not add useful information for the particle characterization.

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2. Heinemann, K., Avalos-Borja, M., Poppa, H., and Yacamán, M.J., Electron Microscopy and Analysis 1979, Conf. Series No. 52, 1980, p. 387.
3. M. Gillet and A. Renou, Surface Science, 90, 91 (1979).
4. M.J. Yacamán (Inst. de Física, U.N.A.M., Mexico), Private communication.
5. A. Howie, in "Modern Diffraction and Imaging Techniques in Materials Science" Edited by" A. Amelinckx, R. Gevers, F. Remaut and J. Van Landuyt, North-Holland, 1970.

(2) In-situ Formation of Clean, Single Crystal, and Electron Transparent Sapphire Substrates

Professional Associates: R. Anton, H. Poppa

We have developed and refined two related techniques to produce electron-transparent films of $\alpha\text{-Al}_2\text{O}_3$ (sapphire) which are clean and exhibit grains of various crystallographic orientations. Both

techniques use a 1000 Å thick film of amorphous Al_2O_3 , obtained by electrolytic oxidation of aluminum foil and subsequent chemical separation from the metal, mounted on a 200 mesh W grid in the hot stage of the uhv specimen chamber of a 100 KV TEM equipped for in-situ experimentation (1). The first method is based on electron beam flash-heating with a 5-50 μm diameter beam at several A/cm^2 current density, which produces sapphire regions of 5-100 μm in size with several large grains. The size of the recrystallized areas increases with increasing duration of the flash (0.1 sec. to 1 sec.) and increasing beam current and diameter. According to Chang (2) and our in-situ nucleation results with metal deposits, the sapphire surface is atomically clean after such high temperature treatment. Thermal preheating of the amorphous film up to 800°C produced very fine polycrystalline Al_2O_3 , but has no apparent effect on the result of subsequent e-beam recrystallization.

We have also produced sapphire films by high temperature (>1200°C) thermal annealing (3), without aid of the electron beam, using a grid type specimen heater. Such films are essentially identical to the center regions of e-beam recrystallized areas. In the outer regions, the 3-beam flash-heating method preserves the original surface relief structures of the amorphous Al_2O_3 film.

Electron-beam recrystallization of Ta_2O_5 , TiO_2 , and ZrO_2 , earlier reported by Francombe (4) was also successfully accomplished, but it essentially failed in the case of SiO_2 .

We acknowledge the contribution of Dr. L. B. Garmon and Mr. H. K. Kim in the recrystallization of Ta_2O_5 , TiO_2 , and SiO_2 , and ZrO_2 , respectively.

Reference Publications:

1. R. D. Moorhead and H. Poppa, Proceed. 27th EMSA Meeting, p. 116; K. Heinemann, D. B. Rao, and D. L. Douglass, Oxid. Met. 9 (1975) 379.
2. C. C. Chang, J. Vac. Sci. Technol. 8 (1971) 500.
3. E. H. Lee and H. Poppa, J. Vac. Sci. Technol. 14 (1977) 223.
4. M. H. Francombe, A. J. Noreika, and S. A. Zeitman, Sect. 6, Final Technical Report, Contract AF 33 (615-3814), BPSN-No.6-684150-415002, 1960.

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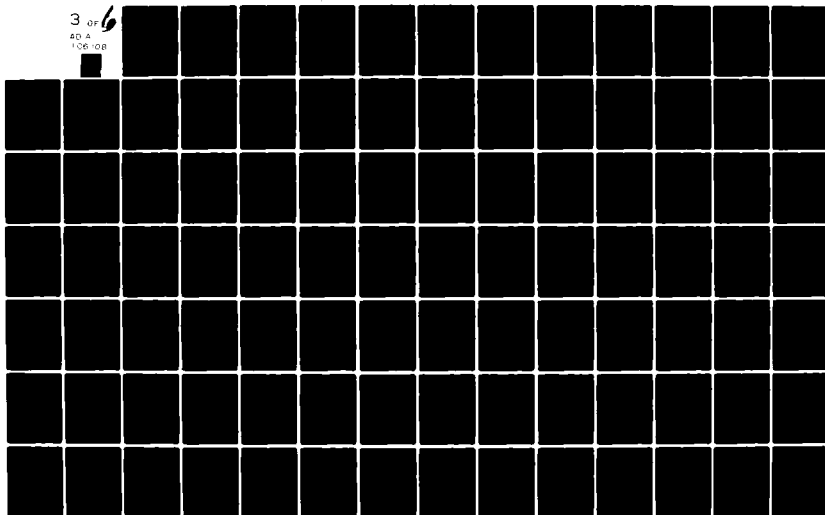
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(3) TEM In-situ Epitaxy on Recrystallized Sapphire Substrates

Professional Associates: R. Anton, H. Poppa

The suitability of freshly recrystallized clean and well ordered alumina films (1) for meaningful and reproducible in-situ studies of the nucleation, growth, and epitaxy of vapor-deposited materials was investigated, using Au, Ag, Fe, Pd, Mo, and W as deposit materials.

The highest density was typically found, as expected, in the polycrystalline substrate area; a lower particle number density, along with decoration of surface relief structures (1), was noted in the sapphire grains near the boundary with the polycrystalline film; and the density is lowest on a (0001)-oriented α - Al_2O_3 grain if it is also close to the center of the recrystallized area. Gold, palladium, tungsten, and molybdenum nucleated epitaxially on (0001)-sapphire faces at elevated temperatures, but for Pd, W, and Mo the crystallite habits were much less pronounced than for gold, whereas the habits of iron and silver were almost as perfect as for gold.

Simultaneous observation of nucleation and growth on other oriented sapphire surfaces, such as less frequently found (1 $\bar{1}$ 02) grains, clearly indicated a generally lower degree of epitaxy and less defined particle shapes. This was observed also for substrate areas near the single crystalline/polycrystalline boundary, which may further attest to increased contamination and/or defect concentration in those regions.

Recrystallized alumina films are also ideal substrates for in-situ studies of supported particle/gas reactions, including catalytic reactions. As an example, we investigated the oxidation of Fe-crystallites, deposited at 600°C on (0001) sapphire.

The oxidation was found to occur at different rates on different faces of the iron particles. Oxidation and annealing at higher temperatures produced α - Fe_2O_3 and $\text{Fe Al}_2\text{O}_4$, respectively, both perfectly epitaxial on the sapphire (2).

Reference Publications:

1. K. Heineman, R. Anton, and H. Poppa, Proceed. 1981 EMSA Meeting, to be published.

2. R. Anton, K. Heinemann, and H. Poppa, Proceed. Int. Vac. Congr. Cannes, 1980.

(4) In-situ Low-Pressure CVD of Silicon and Sapphire

First results have been obtained in in-situ TEM (100 KV) deposition of silicon on electron-transparent sapphire substrates by low-pressure (≈ 1 torr) chemical vapor deposition of SiH_4 . The experiments were conducted inside a cryopumped custom stainless steel specimen chamber of a Siemens Elmiskop 101 TEM, evacuated to the low 10^{-8} torr range. The specimen was kept at temperatures between 900 and 1000°C and e-beam recrystallized immediately prior to admitting silane. The nucleation and growth of silicon was monitored in-situ on the TV monitor of an image intensifier and recorded simultaneously on videotape.

Silicon was found to nucleate at high particle number densities (10^{11} cm^{-2}). The particle density decreases steadily, mainly by growth coalescence.

(5) A Comparison of Smoothing Methods Applied to Electron Energy Distribution

Professional Associates: M. Prutton, L. A. Larson
Graduate Students: K. S. Yu, B.B. Pate

Data fitting routines utilizing 9-point least squares quadratic, stiff spline and piecewise least squares polynomial methods have been compared on noisy Auger spectra and linescans. The spline smoothing technique has been found to be the best, allowing information to be extracted at close to unity signal to noise ratios.

(6) Techniques for the Correction of Topographical Effects in Scanning Auger Electron Microscopy

Professional Associates: M. Prutton, L. A. Larson, H. Poppa

A number of methods for correcting topographical contrast in Auger images and line scans have been tested, using etched silicon substrates covered with gold or silver. The etching produced 13 well-defined angles of incidence on each pyramid. If N_1 electrons were counted at

the energy of an Auger peak and N_2 are counted in the background above the peak then N_1 , $N_1 - N_2$, $(N_1 - N_2)/N_2$, and $(N_1 - N_2)/(N_1 + N_2)$ were measured and compared as methods of eliminating topographical contrast. The latter method gives best contrast compensation, but it can be further improved by utilizing a measurement of the sample absorption current.

Publications During Report Period

1. R. Anton, K. Heinemann, and H. Poppa, The Nucleation, Growth, and Oxidation of Iron Particles on α -Alumina, Proceed. Int. Vac. Congr., Cannes, 1980.
2. M. Avalos-Borja and K. Heinemann, Spacings and Intensities of Weak-Beam Dark Field Thickness Fringes, Proceed. EMSA 1981, in print.
3. R. Anton, H. Poppa, and K. Heinemann, TEM In-Situ Epitaxy on Recrystallized Sapphire Substrates, Proceed. EMSA 1981, in print.
4. K. Heinemann, R. Anton, and H. Poppa, In-Situ Formation of Clean, Single Crystal, and Electron-Transparent Sapphire Substrates, Proceed. EMSA 1981, in print.
5. M. Avalos-Borja, The Selection of Beams for Multi-Beam Dynamical Theory Calculations Used for Weak-Beam Dark-Field Image Interpretation, Proceed. EMSA 1981, in print.
6. K. S. Yu, M. Prutton, and B. B. Pate, A Comparison of Smoothing Methods Applied to Electron Energy Distributions and Auger Linescans, submitted.
7. R. Anton and K. Heinemann, In-Situ Observations of Different Growth Modes of Small Iron Particles of Sapphire, Proceed. EMSA 1980, Claitor's Publ. Div., p. 402.
8. H. Poppa and K. Heinemann, Basic Studies in Catalysis, Optik 56 (1980) 183.

27. PHYSICAL AND CHEMICAL PROPERTIES OF INTERFACES IN SILICON TECHNOLOGY

C. R. Helms, Adjunct Professor, Electrical Engineering

Graduate Students:

R. W. Barton
P. W. Lew
S. C. Perino
J. W. Rouse
M. Taubenblatt

Agency Support:

ARPA MDA 903-79-C-0257
ARMY DAAG 29-80-D-0059
IBM CK 6409437

Technical Objective:

The objective of this program is twofold. First is the measurement and modeling of the important physical and chemical properties of critical interfaces present in silicon integrated circuit technology. A second objective is the development of new techniques and refinement of existing techniques for studies of this type where depth resolutions of the order of 1nm are required.

Approach:

The approach of this program is to attack problems associated with interfaces present in silicon technology from an interdisciplinary point of view. Specifically we are coupling activities in integrated circuits processing technology with those in silicon materials science and interface physics. Using this approach we are able to obtain a more global view of a particular system than would be possible from just one discipline. This approach has been made possible by strong coupling to other groups especially those of W. E. Spicer and J. D. Plummer.

1. Dopant Segregation at the Si/SiO₂ Interface

Graduate Student: Roger W. Barton

Using Auger sputter profiling, we have shown that dopant impurities in silicon can segregate in equilibrium fashion to the Si/SiO₂ interface. This segregation can have important consequences for the procedures used to incorporate dopants into the active regions of silicon integrated circuits. We have studied how the dopant segregation depends on processing parameters such as temperature and bulk doping level. The interface concentrations can be related to both variables using a simple expression:

$$C_I = C_B \cdot A \cdot \exp(-Q/kt)$$

We have verified the linear dependence on bulk doping level ($C_I \propto C_B$) and the exponential dependence on temperature for phosphorus segregation to the interface. The temperature dependence shows that phosphorus has a heat of segregation of 0.26 eV. Arsenic also segregates to the Si/SiO₂ interface to a degree that is quantitatively similar to the phosphorus segregation. We have modeled both segregation phenomena with simple atomic models in the Si/SiO₂ interface. We have also solved diffusion equations which show how the interface segregation can effect dopant distributions in the silicon during the initial stages of oxidation.

2. Auger Sputter Profiling Study of Refractory Metal Schottky Barriers on Si

Graduate Student: Peter W. Lew

The electrical behavior of Schottky barrier diodes depend critically upon the impurity content, interface chemistry, and interface morphology. These interfacial properties of the metal-semiconductor junction are, in turn, determined by processing parameters. To understand the relationship between the electrical properties and the interfacial microstructure, high-resolution Auger sputter profiling (ASP) has been performed on refractory metal Schottky-barrier and related structures, for which previous electrical data was available.

The studies reported here represent a continuation of work begun last year. The emphasis has shifted to include studies of electron-beam (e-beam) deposited Ta-Si Schottky barrier structures for comparison with previous studies performed on sputter-deposited tantalum-silicon and tantalum oxide-silicon samples. In addition, studies of the initial stages of Schottky barrier formation for the Ti-Si system have begun.

Five types of Ta-Si samples were prepared under various processing conditions at IBM (East Fishkill Facility) on chemically cleaned n-type (100) Si substrates. The details of the sample preparation of the sputter deposited Ta/Si and Ta/Ta_xO_y(thin)/Si samples are presented elsewhere.¹ Three kinds of e-beam deposited samples were fabricated. One was not processed with photoresist before e-beam evaporation of Ta from a new Ta charge. A second sample also was not processed with photoresist, but had Ta evaporated from a used charge. On the third sample, photoresist was applied, exposed, developed and removed prior to Ta evaporation from a used charge.

One goal of this study was to determine how the various processing conditions affect the bulk and interfacial impurity content (oxygen and carbon) in the as-deposited samples. Another goal was to determine how a low temperature (400-500°C) anneal in vacuum (10⁻⁶ torr) affects these impurities. The results of the latter objective are particularly important since a low temperature anneal in an inert or hydrogen-containing ambient is normally required to form reproducible Schottky barrier structure.

The major new findings of this study are:

- (1) The bulk of the sputter-deposited and e-beam deposited Ta films contains $\lesssim 3$ at.% O. At the Ta/Si interface of the sputter-deposited sample, there is an increase in the O concentration. Such an increase is not present in the e-beam deposited samples.
- (2) E-beam deposited Ta films also contain ~ 0.3 at.% C in the bulk and a much larger amount at the interface ($\sim 1-3$ at.%). Processing without photoresist and with a used charge leaves the least amount of C (1 at.%).

Processing with photoresist and a used charge leaves the most interfacial C (3 at.%). This residual C left from the photoresist remains intact after an anneal of 400°C for 1 hr. in vacuum.

- (3) Upon annealing the " $\text{Ta/Ta}_x\text{O}_y/\text{Si}$ " sample at 400°C in vacuum for 1 hr., some of the O in the oxide layer diffused away from the Ta-Si interface and redistributed itself uniformly throughout the Ta layer. Greater redistribution occurred for more severe annealing at 450°C for 3 hrs.

These findings have allowed us to construct a preliminary model for the metal/silicon interface which well describes the electrical properties of so prepared devices.

Work has begun on the study of Ti films on Si. These samples were prepared in the Auger analysis chamber by evaporating Ti from a W filament onto sputter-cleaned and annealed n-type (100) Si. It is found that the (2 x 1) Low Energy Electron Diffraction (LEED) pattern, characteristic of clean, well-ordered (100) Si, is maintained for Ti coverages less than one monolayer. No change is observed when the Ti/Si sample is heated to about 450°C for 10 minutes in vacuum. Future work will include additional studies of titanium-silicon interactions.

Reference Publication:

1. T. M. Reith and P. J. Ficalora, J. Vac. Sci. Technol. 16, 303(1979).
3. The Interaction of AsH_3 with the Si(100) Surface
Graduate Student: S. C. Perino

In this part of the program we are investigating the interaction of arsenic with atomically clean silicon surfaces. A detailed characterization of these processes is of considerable interest because it will provide critical information on numerous practical processes and problems encountered in the silicon integrated circuit processing. The significance of these ultra-high vacuum studies can be directly related to the practical concerns of dopant incorporation during chemical vapor deposition and the electrical activity of dopants segregated

at interfaces. During the past year, one area of significant progress has resulted in a quantitative understanding of the adsorption of arsenic from arsine gas. The adsorption was studied over a wide temperature range and the blocking of arsenic adsorption by coadsorbed hydrogen was characterized. By combining the adsorption information with desorption information obtained and reported in the prior year, a firm basis was established to aid in defining the conditions required to achieve bulk crystal doping. The segregation and electrical properties of dopants at interfaces is also a critical problem. The details of the process depends on the particular interface involved (silicon-silicon dioxide, silicon-silicon (grain boundaries), silicon-metal, or silicon-vacuum). The advantage of the silicon-vacuum (free surface) interface is the ready application of standard surface sensitive analytic techniques including Auger electron spectroscopy (AES), Auger Sputter Profiling (ASP), low energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS) and thermal desorption spectroscopy (TDS).

The effect of high concentration of arsenic on the silicon electronic structure has been studied. An arsenic surface layer is electrically inactive as a dopant because of strong interaction with the silicon surface states, but subsurface arsenic is electrically active and dopes the silicon n-type. The studies in this program may also prove useful in understanding related effects such as autodoping and Schottky barrier formation. The following report is divided into four paragraphs dealing with arsenic adsorption, desorption, incorporation and electrical properties.

The understanding of the adsorption of arsenic from AsH_3 as a function of sample temperature and gas pressure has proceeded to the point that it is possible to describe the adsorption process in a quantitative manner with linear, first-order rate equations. Qualitatively, the adsorption can be understood as a combination of two steps: (i) adsorption of AsH_3 and decomposition into arsenic and adsorbed hydrogen (ii) desorption of the adsorbed hydrogen. Experimentally, these processes are observed by monitoring the arsenic coverage with AES as a function of

time at a fixed sample temperature and gas pressure. A fast initial adsorption occurs, which corresponds to the first step, followed by a much slower rate of adsorption which is controlled by the second step. At lower temperatures where the hydrogen desorption rate is small, the hydrogen occupies a substantial fraction of the fixed number of adsorption sites and inhibits arsenic adsorption. The hydrogen poisoning of adsorption sites results in a slow arsenic adsorption rate which is largely independent of gas pressure. The fast adsorption is characterized by the sticking coefficient parameter and is defined to be the constant of proportionately between the adsorption rate and the gas flux in the low coverage limit. The sticking coefficient has been measured to be .04, .02, .02 and .05 and, at room temperature, 300°C, 400°C, and 500°C respectively. At 700°C the hydrogen desorption rate is large and the slow adsorption process is not observed. The saturation arsenic coverage at high temperatures is estimated to be about 10% of the surface.

The diffusion of the surface arsenic into the bulk of the crystal was achieved by annealing for long times in an AsH_3 background and was investigated with ASP. Various arsenic surface layers obtained with a minimum of high temperature treatment were profiled in order to characterize profile broadening processes resulting from the ion milling technique. The shape of the diffusion profile consists of a shallow initial region about 10 Å deep with a steep slope which is attributed to the surface arsenic layer, and a deeper region with a more gentle slope. The arsenic concentration in the bulk is obtained by subtracting the profile of the surface layer from the diffusion profile. The diffusion depth, defined to be that distance at which the arsenic concentration is 10% of the initial concentration, was measured as a function of sample temperature and AsH_3 pressure during 30 minute anneals. It was found that at a given pressure there exists an optimum temperature that maximizes the diffusion depth. At temperatures below the optimum temperature the diffusion rate is too low and at temperatures above the optimum temperature the desorption rate is too high. Since the adsorption and desorption rates are known as a function of temperature and surface coverage, a relationship can be derived giving the

pressure required at a given temperature in order to achieve surface saturation and maximize the dopant incorporation. After diffusing the arsenic into the bulk, high temperature treatments of very short duration were tried as a means of vaporizing the surface arsenic layer while leaving the arsenic in the bulk without arsenic at the surface, suggesting a strong surface segregation effect.

The adsorption of AsH_3 and the influence of high concentrations of arsenic on the silicon electronic structure were investigated with UPS at photon energies of 10.2 eV and 21.2 eV. The hydrogen influence can be separated from the arsenic influence by comparing UPS spectras with both species on the surface to UPS spectras with only arsenic on the surface. Hydrogen attenuates the silicon surface states and decreases the work function by 0.4 eV. A saturated surface layer of arsenic without hydrogen can be obtained by a short AsH_3 exposure at 700°C. The emission intensity increases strongly at a binding energy of 2 eV. Arsenic on the surface hybridizes with the surface states and removes them from the gap, but does not increase the work function. Although the Fermi level at the surface is no longer pinned by the surface states, the surface arsenic does not dope the crystal. However, sub-surface arsenic obtained by annealing at high temperature strongly dopes the surface n-type. Since the shift in the bulk Si photoemission peaks is larger in spectra taken at the more surface sensitive 21.2 eV photons, the bands bend from their p-type bulk positions downward at the surface. Under the proper conditions the silicon surface can be doped n-type with small AsH_3 exposures.

4. Studies of HCl/O_2 -Grown SiO_2

Graduate Student: J. W. Rouse

(Fairchild work in conjunction with Dr. Bruce Deal)

Researchers have recently found that the inclusion of HCl in an oxidizing ambient produces SiO_2 layers with desirable properties. The reproducibility of oxide breakdown voltage is increased, and there is a reduction of mobile alkali ions. The behavior of chlorine in growing the oxide may also provide insight into the kinetics of the oxidizing

species since both Cl and oxygen are believed to enter the oxide as negative ions.

Work related to these HCl/O₂-grown oxides has followed two tracks: (1) Auger sputter profiling (ASP) and secondary ion mass spectrometry (SIMS) studies of the chlorine distribution; (2) effects of the Auger primary electron beam. Both of these will be briefly summarized.

Our studies have revealed, in agreement with other work,^{1,2} that chlorine in an HCl/O₂-grown SiO₂ layer piles up on the oxide side of the SiO₂/Si interface. We have used ASP to determine the total amount of interface chlorine in SiO₂/Si structures fabricated at Fairchild Semiconductor, Palo Alto. We have studied Cl pileup at the SiO₂/Si interface as a function of growth time, temperature, and HCl partial pressure. These studies have revealed a monotonic increase of interface chlorine as a function of growth time for fixed values of temperature and HCl partial pressure.

In addition to ASP studies, we have performed secondary ion mass spectrometry (SIMS) analysis on these same samples. SIMS provides a superior sensitivity (with a depth resolution inferior to ASP), and has enabled us to determine bulk oxide chlorine concentrations. We have found that the transport of chlorine through the oxide is driven by a large electrochemical field with a potential drop of approximately 0.65 eV for our samples. Subsequent application of general transport equations in a steady state analysis has allowed us to accurately model chlorine flux and concentration.

The second aspect of this work has been the study of the effect of the Auger primary electron beam on the chlorine distribution. We used thermally grown SiO₂ samples implanted with chlorine to determine to what extent the measured chlorine profile was subject to distortion by the electron beam. We compared these effects by sputtering or etching samples to various depths before turning on the primary electron beam. These studies revealed that the electron beam swept chlorine to the SiO₂/Si interface in an amount roughly proportional to the total electron beam exposure time. Quantitative analysis allowed us to predict the size of this effect, and we determined that the role of electron

beam effects in producing chlorine pileup in the Fairchild samples was not a major one.

We have analyzed the profile distortion due to electron beam effects by numerically solving the time-dependent diffusion equation, where the transport parameters depend on the electron beam parameters. In this way we have obtained a good agreement between this model and our data. We conclude that the electron beam initiates transport by somehow activating the chlorine atoms.

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5. Photoemission Studies of Silicide Formation and Schottky Barrier formation in Ti-Si and Ti-Surface Contaminant-Si Systems

Graduate Student: Marc Taubenblatt

The use of metal silicides as Schottky barriers, ohmic contacts, and low resistivity high temperature stable interconnects has become increasingly important in the integrated circuit industry. The formation and ultimate electrical properties of these circuit elements are dependent on impurities and surface contaminants present when the metal to be reacted is deposited. The purpose of this work is to characterize silicide formation under UHV conditions, with controlled surface contaminants (O_2 , SiO_2 , C) present.

To date, four types of samples have been studied by evaporating thin layers of Ti metal, and annealing at successively higher temperatures, while observing electronic and chemical changes with Photoemission and Auger spectroscopy: (1) clean(100)Si (2) adsorbed O_2 on clean Si(100) (3) thin layer of SiO_2 on clean Si(100) (sputter induced, boiled in H_2O) (4) clean SiO_2 (thermally grown dry O_2).

The silicon samples were n-type (100) IC grade wafers with $\sim 5 \times 10^{16}/\text{cm}^3$ phosphorus doping. The surface was cleaned by sputtering with neon gas and annealing at $\sim 900^\circ\text{C}$. Ti metal was evaporated by e-beam heating to a thickness of ~ 3 to 30 \AA .

The major findings are for each of the samples is as follows:

1. Clean Si

- (a) In contrast to many other metals, Ti deposited on Si at room temperature forms a relatively sharp interface.
- (b) The presence of Ti quenches the intrinsic surface states, induces extrinsic surface states just below the Fermi level, and does not change the Fermi level pinning.
- (c) Low temperature ($400\text{--}500^\circ\text{C}$) anneals cause intermixing of the Si and Ti near the interface, forming what appears to be a silicide.
- (d) Higher temperature anneals ($700\text{--}950^\circ\text{C}$) cause substantial dissolution of Ti into the Si substrate.

2. Adsorbed O_2 on Clean Si

- (a) Evaporated Ti interacts strongly with the adsorbed O_2 , as evidenced by the reduced emission of electrons from the Ti 3d states. In addition the adsorbed oxygen appears to distribute itself throughout the Ti film.
- (b) Annealing produces substantially the same results as for clean Si, with the O desorbing from the Ti film at $\sim 600^\circ\text{C}$.

3. Thin Layer of SiO_2

- (a) Ti appears to react less strongly with the O than in the adsorbed case.
- (b) Annealing at low temperature caused the formation of silicide phases coexisting with SiO_x phases.
- (c) At higher temperatures Ti diffused into the bulk Si, while the SiO_x remained at the surface. Eventually the SiO_x sublimed into vacuum.

4. Thermally Grown SiO_2

- (a) Ti appears to react less strongly with the O than in the adsorbed case.

- (b) Low temperature anneals produce little change in chemistry.
- (c) High temperature anneals cause the apparent formation of TiO_x at the surface, which is stable to $>800^\circ C$.

Future work will investigate the role of oxygen in determining Schottky barrier height, and treat carbon contamination in a similar manner.

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28. ELECTRON-DENSITY APPROACH TO BINDING ENERGIES OF MOLECULES AND
CONDENSED SYSTEMS

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Technical Objective:

To develop a new technique for estimating the ground-state electronic energy of an arbitrary configuration of atoms, that will be accurate enough to give useful results, and at the same time significantly less laborious computationally than existing methods that involve the self-consistent determination of many-electron wave functions.

Approach:

Ways of approximating the ground-state energy of a many-electron system in terms of the electron density distributions are being explored. The long-familiar Fermi-Thomas method does this, but is far too inaccurate to be useful for detailed calculations. The accuracy can be greatly improved if, in addition to the often-studied "gradient corrections," functionals of the density are employed that are fully nonlocal, i.e., that depend on the entire form of the density distribution, rather than being integrals of a function of the local density and its derivatives.

Research Report:

The kinetic energy of a many-electron system has been separated into two parts, each positive and usually of comparable magnitude. One of these is easily computable from the charge density, but the other has a number of general properties (lack of smoothness, extreme nonlocality, etc.) that cause most simple schemes for approximating it to fail in various limiting cases. Some of the more promising schemes have been studied numerically on several one-dimensional examples, and have proved unsatisfactory. Current attention is being directed at other approximation schemes that will be simple to implement in three-dimensional problems.

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29. STRUCTURAL STUDIES USING SYNCHROTRON RADIATION

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Research Report:

(1) Single Crystal X-ray Absorption Spectroscopy Studies

Structural determination by x-ray diffraction requires long range order in the sample. One of the primary advantages of the extended x-ray absorption fine structure (EXAFS) technique is that the absorbing atom need not be oriented in an extended array or lattice. Most of the x-ray absorption studies done heretofore have taken advantage of this freedom, measuring spectra for randomly oriented samples in solution, as powder, or as amorphous materials. The synchrotron radiation emitted from an electron storage ring is, however, linearly polarized in the horizontal plane, and is well suited for use in absorption studies of oriented single crystals. The combination of oriented sample and polarized beam permits determination of the angular dependence of the absorption spectrum. The polarization effects can thus provide angularly selected structural information since the x-ray absorption spectrum contains information about

the distances to, numbers of, and types of atoms surrounding the absorber.

We have been engaged in a series studies to demonstrate the use of these effects. A study of the orientational dependence of the Mo K-edge absorption spectrum of ammonium dithiomolybdate, $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ has been completed. The case of dithiomolybdate chosen for this study is particularly illustrative because the spectra from different orientations can be compared with those of molybdate and thiomolybdate which have been previously studied in experimental and theoretical detail (1). In addition, the shape of the edges for different angles between the dithiomolybdate molecule and the polarization vector can be interpreted using molecular orbitals calculated from the self-consistent field X-alpha multiple scattered wave (SCF X-alpha MSW) formalism, which we have described earlier (1).

Following the collection of spectra with the polarization vector parallel to the oxygen-oxygen interatomic vector, the sulfur-sulfur vector, and the two-fold rotation axis, self-consistent field X-alpha multiple scattered wave (SCF X-alpha MSW) calculations were done to interpret the observed orientation dependence. It is clearly shown that this orientation dependence can be used to highlight the edge features which derive from molecular orbitals contributed to principally by the oxygen or the sulfur ligands. Anisotropy is also apparent in the extended x-ray absorption fine structure (EXAFS) spectra, which were recorded for orientations along the S-S and O-O interatomic vectors (2). Polarized single crystal x-ray absorption spectroscopy can provide orientationally selective information about the absorbing atom. Thus it could, in principle, be used to deduce certain types of geometric information about the x-ray absorbing species.

(2) Rapid X-ray Absorption Spectroscopy Using Dispersive Methods

A conceptually different approach to obtaining EXAFS data is being developed which should increase the efficiency of data collection and minimize the effects of beam instabilities. Polychromatic radiation is used to record a complete EXAFS spectrum simultaneously in a dispersive mode rather than measuring point-by-point which is the technique used at

present. We utilize a cylindrically bent Si(111) crystal (capable of providing energy ranges of greater than 1000 eV) to disperse the quasi-parallel polychromatic beam. This energy dispersed beam converges to a focus at the sample position; the beam transmitted through the sample then diverges towards an x-ray detector. The position of the beam, incident on the detector, can be correlated to energy.

During the past year an energy dispersive EXAFS camera has been designed and built (3). This camera utilizes a triangular crystal bender of our own design, which is mounted on a motor-driven Huber goniometer. This goniometer is used to accurately orient the crystal to the desired angle with respect to a direct x-ray beam. The crystal bender can also be rotated about a horizontal axis so that crystal glitches can be shifted in energy away from the critical region of the EXAFS spectrum. The sample and detector are mounted on an optical bench which can be rotated about a vertical axis which is co-axial with the Huber goniometer axis. Fine X-Y slits are used to both define the incident beam and to reduce the background scattering. An electronically-controlled shutter has been incorporated so that timed exposures can be made. A flat mirror was added to eliminate the harmonic component of the energy dispersed beam. A kinematically located base plate permits fast alignment to the x-ray beam.

Spectra have been recorded using film and with a photodiode array (Reticon) detector. We have observed excellent resolution (comparable to that obtainable with conventional EXAFS scans) and have recorded complete spectra in times as short as about 100 msec. These studies, some of which were on very dilute solutions (less than 10 mmolar) lead us to believe that it will be possible to measure EXAFS spectra in systems under a dynamic conditions. Such studies are being planned.

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30. SOLID STATE IONICS

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Technical Objectives:

SOLID STATE IONICS

- (1) Development of new materials for use in solid state electrochemical systems. This involves design, synthesis and characterization of inorganic materials as well as evaluation of their structure and various thermodynamic and kinetic properties.
- (2) Achievement of understanding concerning the important phenomena involved in the rapid transport of ionic and electronic species in solid electrolytes and mixed ionic-electronic conductors, and their structural basis.

- (3) Development of relevant experimental and theoretical techniques for the evaluation of thermodynamic and kinetic properties of molten salts and solids with mobile ionic species.
- (4) Investigation of various areas of potential application of solids with fast ionic transport, such as materials and phenomena involved in high performance battery and fuel cell systems, catalysis, selective ion sensors, electrochromic display devices, hydrogen storage, etc.

MATERIALS PREPARATION METHODS

Investigation of new techniques for materials synthesis and the preparation of special microstructures. This includes electrocrystallization of metals, alloys, semiconducting materials, and metal-metalloid compounds from molten salts and other electrolytes. The synthesis of metals and ceramics by the decomposition of infiltrated polymeric precursors, as well as the preparation of materials in thin film form by evaporation, sputtering, and reactive sputtering methods are also being pursued.

Research Report:

(1) Lithium-Based Electrochromic Materials

A program of research has been undertaken to investigate the possibility of using the color change observed on electrochemical injection of lithium into some transition metal compounds as a display device. The ultimate objective is to develop an all solid state system. This program involves the search for new electrochromic materials with very high lithium diffusion rates and the development and use of equilibrium, steady-state and transient electrochemical techniques for the assessment of their utility. Work to date has shown that some ternary phases with certain crystal structures can have very fast kinetics. Efforts are being made to develop methods for their synthesis in thin film form.

(2) Materials for Advanced Lithium Batteries

Theoretical models have been developed and experimental measurements

made of the defect structure and ionic and electronic conductivity in several groups of solids with highly mobile atomic species which might be useful as solid electrolytes or electrode materials in new types of battery systems. Particular attention has been devoted to materials with crystal structures containing crystallographic tunnels and sparsely populated sites. These have included beta alumina, alkali metal ferrocyanides, titanates, germanates, silicates, phosphates, ternary oxides, aluminosilicates, fluorides, nitrides and related materials.

Current work on solid electrolytes concentrates on materials which show very high lithium ionic conductivity at ambient and elevated temperatures. Materials include solid solutions with tetrahedral anionic groups and crystal structures related to lithium orthosilicate and lithium phosphate which have high conductivities at about 400°C, the temperature of interest for some advanced lithium batteries. A second material of importance is lithium nitride, which has a layer type crystal structure with very high lithium ion conductivity at low temperatures. While this behavior is very anisotropic, it has been found that appropriate control of the microstructure can produce polycrystalline bodies with very high lithium ionic conductivity values at ambient temperatures, close to those in the "fast" direction of single crystals. Other materials include doped lithium iodide, alkali metal aluminum halides, and a number of pure and doped materials with the anti-fluorite structure.

In addition to this work on solid electrolytes, a new low temperature molten salt has been discovered which can be used in the presence of elemental lithium and lithium-rich metallic alloys in both primary and secondary (rechargeable) batteries with high specific energies. This salt causes the formation of a very thin stable layer of a lithium solid electrolyte on the lithium surface, which prevents direct chemical reaction, and yet allows electrochemical reaction between the electrode and the electrolyte with

very little impedance and overvoltage. While this electrolyte has the very great advantage that it makes it possible to produce reversible lithium electrodes at moderate temperatures, as well as a number of other very attractive attributes, its practical importance has not yet been evaluated. Work is being undertaken to measure its thermodynamic stability range as well as other properties relevant to its use in lithium-containing cells. The behavior of a number of potential electrode materials in high voltage cells with this electrolyte is being studied.

Work is also being done to develop the theoretical and experimental tools to evaluate potential electrode materials for use in this and other systems. A new galvanostatic intermittent titration technique has been developed to evaluate the chemical diffusion coefficient and other kinetic parameters of mobile ionic species in mixed ionic-electronic conductors. This method is especially powerful when used in conjunction with coulometric titration, which allows the composition of both polycrystalline and single phase samples to be changed quantitatively, thus avoiding reproducibility and analytical problems normally encountered in the production of a series of separate samples of different compositions. By these means, both thermodynamic and kinetic data can be obtained on appropriate materials with an unusual combination of precision and compositional resolution. Especially interesting is the ability to evaluate thermodynamic quantities, such as the free energy of formation, as a function of composition within narrow intermediate phases. Likewise, kinetic quantities such as the chemical diffusion coefficient, self diffusion coefficient, partial ionic conductivity, and tarnishing rate constant can be obtained as functions of the stoichiometry - and thus defect concentrations - in narrow phases.

These techniques have been applied to the lithium-aluminum and lithium-silicon negative electrode materials, as well as to a number of other lithium binary systems. A group of new positive electrode materials have also been studied, including several ternary oxides, sulfides and nitrides.

A novel approach to electrode structures has also been demonstrated, whereby all-solid electrode structures can be produced which may have kinetic properties comparable to those typically found in traditional very fine particle size powdered electrodes. The important feature in this case is the use of a composite microstructure containing finely dispersed reactant phases in a metallic matrix composed of a material with a very high chemical diffusion rate of the electrochemically reactive species, eg. lithium. Work under this program has led to the identification of several candidate matrix materials which have the requisite thermodynamic and kinetic properties. Initial experiments have demonstrated that electrodes fabricated following this approach behave as predicted. The possibility of the development of all-solid electrode structures rather than traditional powder-containing structures, presents some attractive alternate possibilities for battery and fuel cell design and fabrication. This may also lead to electrodes with a microstructurally reversible internal morphology, and hence true reversibility, a long sought-after goal.

(3) Electrodeposition from Molten Salts

Theoretical and experimental work are underway on the use of electrochemical techniques for the growth of both single crystals and polycrystalline materials, as well as for the preparation and purification of selected materials. Of special current interest is the inexpensive preparation of silicon by electrocrystallization from molten salts.

(4) Use of Solid State Ionics to Influence Heterogeneous Catalysis

It has been shown that electrochemical cells involving solid electrolytes and mixed ionic-electronic conductors can be used to control the concentrations of specific species at solid-gas interfaces and to greatly influence the rates of heterogeneous reactions.

Experiments have shown that the rate of decomposition of NO can be increased by a factor of a million by the use of solid state ionic

techniques, achieving greater specific reaction rates on certain oxide surfaces than on platinum, the conventional catalyst for this purpose.

Current work is aimed at the extension of these concepts and techniques to influence heterogeneous displacement reactions upon the surface of solids. Significant enhancement has been found in the rate of formation of methane from CO/H_2 and CO_2/H_2 mixtures.

(5) Use of Anion-Conducting Solid Electrolytes in Coal-Consuming Fuel Cells

A novel type of moderate temperature fuel cell for the electrochemical combustion of coal and related carbonaceous materials is being explored. A major feature of this new approach is the utilization of an oxide ion-conducting solid electrolyte and a mixed ionic-electronic conducting liquid matrix material in the negative electrode compartment. A number of materials are being evaluated for their possible use in such systems.

(6) Hydrogen Storage in Solid Hydrides

Work is being undertaken to use the concepts, tools and techniques of solid state ionics to evaluate the pertinent thermodynamic and kinetic parameters of solids for hydrogen storage. This approach will also be used to search for and investigate new possible solid hydride systems.

(7) Condensed Phase Electrodes for Fluoride-Based Galvanic Cells

A new concept is being explored which involves a polyphase liquid system with a very large capacity at quite high fluoride activity. It is expected that this will make it possible to consider the use of fluoride-based battery systems and other high voltage galvanic cells that have not heretofore been feasible because of difficulties in handling gaseous fluorine.

(8) Electron Conductivity of Molten Salt Electrolytes

Experiments are being undertaken to evaluate the minority electronic conductivity in molten chlorine and related salts of interest for use in advanced lithium batteries. The influence of temperature, composition, and lithium activity are being investigated, the latter by the use of the Wagner asymmetric polarization technique with one ionically blocking electrode.

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31. ACOUSTIC INTERACTIONS WITH SOLIDS

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F49620-79-C-0217
DOE DE-AT03-81ER10865

Nondestructive Testing

Technical Objective:

To use acoustic techniques to determine the location and size of flaws in materials and determine more subtle properties of materials such as microstructural properties and hardness.

Approach:

Acoustic imaging techniques in which an array of piezoelectric transducers is employed have been shown to produce good images of flaws in metal samples. Related techniques operating at high frequencies are being used to measure and characterize extremely small flaws in ceramics.

Similar techniques are also being developed for surface wave probing of surface cracks and for measurement of microstructure in metals.

Research Report:

We have continued our construction and examination of acoustic imaging systems. A 32 element real-time synthetic aperture digitally processed acoustic imaging system operating at 3.3 MHz center frequencies has been used with a new type of surface wave transducer array to image surface cracks and holes in aluminum and steel. We have also constructed a contacting array to obtain longitudinal wave images in aluminum and steel.

A second computer processed, mechanically scanned, synthetic aperture system has been constructed for detecting and analyzing flaws in ceramics and metals. It operates at a frequency of 50 MHz. We have carried out image reconstructions using from 32 to 256 elements in a complete circle around the cylindrical object to be examined and have obtained good images of holes in aluminum cylinders of 3λ and 4λ respectively (370 μm and 500 μm in diameter).

The experimental system has been built with the main purpose of examining cylindrically shaped silicon nitride ceramics. It is possible to scan a single transducer with an 8 μm accuracy in two directions and rotate the cylindrical sample accurately in the angular direction. Several 50 MHz transducers have been built with excellent operating characteristics for use in this system.

We have used this system for measuring scattering of 5.0 MHz surface acoustic waves from surface cracks in ceramics. We have been able to accurately predict breaking stresses due to cracks induced by machining. Some of these cracks are long and of the order of 25-50 μm deep, others are half penny shaped of the order of 200 μm diameter. We have observed acoustically that many cracks are closed at the top and that plasticity is an important effect in structural ceramics such as silicon nitride. The results we are obtaining are in excellent agreement with the materials properties predicted by Evans and Marshall at Berkeley. This is the first analytic tool that has been available for making such measurements.

We have adapted our stress measurement system to carry out measurements of three-dimensional stress variations. To do this we work in a transmission mode with annular spherical transducers producing and receiving a focused acoustic beam. A pair of coaxial piston transducers produce and receive a parallel beam. The phase difference measured between the two beams depends mainly on the region near the focus of the focused beams. So by this means, we can determine the phase change due to the axial component of stress in regions near the focus.

A new and detailed theory of three-dimensional acoustoelastic stress effects has been worked out. This theory has been used with our experiments on cracked aluminum and steel samples. For the first time three-dimensional variations of stress near a crack in good agreement with our predictions from numerical computations have been measured. The first measurements of residual stress effects due to plastic yield have also been carried out on cracked steel samples.

Other related work on measuring stress and stress intensity factor has been carried out on our Thrust Program on Nondestructive Testing. This is reported separately.

Acoustic Surface Wave Correlators and Convolvers

Technical Objective:

To construct devices which can correlate two electrical signals with each other, take transforms of signals, and act as variable programmable delay lines, and in particular, programmable inverse filters and adaptive filters.

Approach:

We are constructing acoustic surface wave devices on silicon substrates. A sputtered zinc oxide layer is used to provide piezoelectric coupling.

Research Report:

We have described before an acoustic surface wave correlator which employs zinc oxide laid down on silicon. During the year, we have developed our magnetron sputtering system further and have carried out

very complete tests on it using both a pure oxygen atmosphere and argon-oxygen mixtures. Lower temperature depositions with less power for a given deposition rate appear to be possible with the argon-oxygen mixture.

We have developed new techniques for increasing the barrier potential of PtSi on Si Schottky diodes. This involves implantation of a thin boron layer ($< 1000 \text{ \AA}$ thick) before deposition of platinum. The layer moves in front of the platinum layer as it alloys with silicon and increases the barrier potential to as much as 1.0V. The diodes themselves have almost ideal I-V characteristics with a forward current of the form $I = A \exp (qV/kT)$ and $m = 1$ to within 2%.

32. ELASTIC-PLASTIC STRESS ANALYSIS WITH PARTICULAR EMPHASIS
ON METAL-FORMING APPLICATIONS

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and Metal Working
DAAG 29-81-C-0017
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Technical Objective:

In order to be able to predict that a metal-forming process will produce a satisfactory product, free from defects such as internal and surface cracks, high residual stresses or local concentrations of high strain, it is necessary to carry out a complete elastic-plastic stress and deformation analysis of the process. The Thrust Program on Metal-working and Plasticity is concentrating on particular aspects of this area of technology: a.) the finite-element analysis of cold extrusion and comparison of the residual stresses evaluated with acousto-elastic measurements of them, and b.) the finite-element analysis of warm rolling of steels and comparison of the resulting predictions of process characteristics with those observed in rolling experiments. Much of the group's research supports this thrust program and is described in the

Thrust Program on Metalworking and Plasticity contribution to this Annual Technical Report. In the course of that investigation, a basic error was uncovered in the currently accepted elastic-plastic theory for finite deformation. What led to the discovery of this problem and the basic reason for it were presented in a paper generated on the project [1]. Since the development of elastic-plastic theory stimulated by this anomaly falls outside the main scope of the thrust program, this facet of our research is reported separately. The objective of this part of our work is to correct the basic structure of elastic-plastic theory, hence to improve the accuracy of the theoretical evaluation of stress and deformation distributions by ascertaining in what circumstances the approximation involved in the currently accepted approach is adequate.

Approach:

Elastic-plastic analyses and associated computer codes in current use for stress and deformation evaluations involving finite strain and rotation are based on the linear kinematic hypothesis that the total strain rate is the sum of the elastic and plastic strain rates. However, careful definitions of plastic and elastic deformation in conformity with the physical phenomenon give a nonlinear kinematic relation for the total strain rate in which the plastic strain rate term involves coupling with the elastic strain. This arises because plastic flow occurs while the body is stressed, and hence strained elastically, and the contribution of the plastic strain rate to the total strain rate is influenced by the elastic strain present. Elastic-plastic theory has been developed on the basis of the exact kinematics [2] and recently transformed into incremental form [3] which makes it more amenable to application.

Research Report:

In order to illustrate the benefits which this more exact mathematical representation generates, the topic we are now investigating (the choice of stress-rate definition in incremental or rate form of

elastic-plastic theory) is briefly reviewed. Presently, different rate definitions of different stresses are being adopted in computer codes in current use. As pointed out by Prager [4], the combination of the linear kinematic hypothesis for the strain rate and Hooke's law for the elastic strain has insufficient mathematical structure to prescribe more than the need to use an objective stress rate of which there are an infinite number including the Jaumann, Oldroyd, Cotter and Rivlin, and Truesdell definitions. In a recent paper [5], Nemat-Nasser states: "The choice is more a matter of taste and convenience than anything else". On the other hand, Rice [6] has in effect shown that in elastic-plastic analysis the difference between these choices can be of the order of the dominant terms present. When the exact kinematics is used in combination with finite-deformation elasticity theory, the question becomes a purely mathematical one, with each choice of stress rate generating a corresponding unique elastic-plastic operator which relates the rates of stress and total strain. Thus the inconsistency in the deduced elastic-plastic constitutive relations is eliminated.

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33. SUPERCONDUCTIVITY AND MOLECULAR PHYSICS

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Agency Support:

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Technical Objective:

To study the feasibility of obtaining superconductivity at a relatively high temperature in organic and organo-metallic systems. The design and fabrication of microminiature cryogenic refrigerators using photolithographic techniques. The utilization of these for the study of the physical properties of very small crystalline samples. To understand the nature of short and long term memory in neural networks. The development of mathematical tools to handle this problem.

Approach:

Our main line of work is the study of the possibility of high temperature superconductivity using an exciton induced electron-electron interaction rather than the phonon mechanism. Our efforts have centered on linear chain systems where we believe a sufficiently strong excitonic interaction can be obtained with suitable ligands.

We have studied the effects of impurities and imperfections on the various types of ordered phases in quasi-one-dimensional systems and the effects of the resultant localization on superconductivity.⁽¹⁾

An investigation of the feasibility of building microminiature cryogenic refrigerators using photo-lithographic techniques has proved

successful. Techniques have been developed for building counter-current heat exchangers and Joule Thomson refrigerators on these glass plates. A 250 mW refrigerator has been operated at 80K.⁽²⁾ A study of Laminar flow heat exchangers shows that these can be designed for high frequency.⁽³⁾ This, too, has been demonstrated. The prospects of building miniature 20K and 4K refrigerators by this means look good.

Work has continued on the study of the memory storage capacity of a neural network. A linearized approximation of the mathematical description of the problem corresponding to the high temperature expansion of the corresponding Isling model has been solved exactly.⁽⁴⁾ Some progress has been made in the solution of the general problem. We have shown that our model has a holographic-like means for the recall of information from long term memory.

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34. SURFACE REACTIVITY

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Agency Support

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DOE 10490

Overall Technical Objective

To understand the effects of the geometry and composition of metal and metal compound surfaces on chemical reactivity of surfaces.

Acid-Base Displacement Reactions on Ag(110)

M. Barteau

In studying oxidation reactions on Ag(110), we have observed a pattern of reactivity. Preadsorbed oxygen atoms reacted with CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3COOH , HCOOH , C_2N_2 , C_3H_6 and H_2O according to the general reaction scheme $\text{BH}_{(\text{g})} + \text{O}_{(\text{a})} \rightarrow \text{B}_{(\text{a})} + \text{OH}_{(\text{a})}$. In these cases B represents CH_3O , CH_3COO , C_2H , etc. In addition, reactions of the type $\text{H}_2\text{CO}_{(\text{g})} + \text{O}_{(\text{a})} \rightarrow \text{H}_2\text{CO}_{2(\text{a})}$ and $\text{HCOOCH}_3(\text{g}) + \text{O}_{(\text{a})} \rightarrow \text{HCOO}_{(\text{a})} + \text{CH}_3\text{O}_{(\text{a})}$ were also observed. These reactions are analogous to reactions of OH^- in aqueous solution and strongly suggest an acid-base character to the reactions of $\text{O}_{(\text{a})}$. General reaction types suggest both Bronsted and Lewis basicity of $\text{O}_{(\text{a})}$. The relative acidities of the above molecules was determined by reactions of the type

$B'H(g) + B(a) \rightarrow BH(g) + B'(a)$; eg, $HCOOH(g) + C_2H(a) \rightarrow C_2H_2(g) + HCOO(a)$ and its reverse. The order established was $CH_3COOH > HCOOH > CH_3CH_2OH > C_2H_2 > CH_3OH > C_3H_8, H_2O > H_2, C_2H_2, C_2H_6$. The order among the last three species could not be determined. The relative order did not correlate well with either B-H bond dissociation energy or aqueous acidities. The agreement with relative gas phase acidities ($BH \rightarrow B^- + H^+$) was nearly perfect.

Acetylinic Complexes on Ag(110)

M. Barteau

E. Stuve (In collaboration with Dr. B. Sexton, G.M. Research Labs, Warren, Mich.)

Molecular acetylene adsorbs weakly on Ag(110), presumably via π -electron donation. Photoelectron spectra show a slight lowering of energy of the π -orbitals (in UPS) and a strong satellite feature in XPS suggestive of weak chemisorption. The approximate desorption energy determined by temperature programmed desorption is 12 kcal/gmole. When atomic oxygen is preadsorbed, acetylene reacts at low temperatures first to form C_2H which, when heated to 350K, disproportionates to C_2H_2 and C_2 . The C_2 fragments form different ordered structures depending on the initial oxygen coverage. The basic overlayer unit cell appears to be (2x6) structure. Spot-splitting along the close-packed dimension on the surface was indicative of a long range periodicity, possibly due to displacement of the ridge atoms normal to the rows. This carbon structure is unreactive to molecular oxygen. When heated above 550K, C_2 dissociates to adsorbed carbon atoms, the LEED structures revert to (1x1), and the carbon can be oxidized to CO_2 by exposure to O_2 . These intermediates can be positively identified by titration with CH_3COOD to form $C_2HD(g)$ and $C_2D_2(g)$, respectively. Atomic carbon does not react. High resolution electron loss vibrational spectroscopy done in collaboration with Dr. Bret Sexton at General Motors Research Labs gives additional information on the reaction. The absence of a vibrational mode corresponding to the C-C stretch suggests that molecular acetylene, C_2H and C_2 lie with the C-C axis nearly

parallel to the surface. The bonding for the C_2H species is suggested to be similar to that observed by x-ray diffraction for acetylenic complexes of silver.

The Hydrogen-Oxygen Reaction on Pt[9(111)x(100)]: Molecular Beam Relaxation Spectroscopy

G. Gdowski

The catalyzed reaction of hydrogen and oxygen on platinum to form H_2O is a classic reaction for basic studies in heterogeneous kinetics. We have examined this reaction using molecular beam relaxation spectroscopy, in order to measure the rate constant(s) for the surface reaction(s) and further elucidate the reaction mechanism. A stepped platinum surface was chosen so as to provide the possibility of multiple reaction pathways. In this study a constant flux of oxygen was directed onto the surface. Simultaneously, a square-wave modulated H_2 beam impinged upon the surface. The relative fluxes of the two reactants were adjusted so that the oxygen coverage was nearly constant at approximately 0.3-0.5 monolayers. The dependence of the phase and amplitude of the product H_2O desorbing from the surface on temperature and reactant flux was determined. The mechanism of reaction was pronouncedly non-linear with respect to the surface concentration of adsorbed hydrogen atoms, and linear with respect to O-adatom concentration. Isotopic mixing experiments showed that dissociation of H_2 proceeded water formation. Two mechanisms appear consistent with these observations. One of these is the sequential addition of adsorbed H atoms to $O_{(a)}$ to form first $OH_{(a)}$, then H_2O . The second is a concerted reaction of two H adatoms with $O_{(a)}$, similar to an H atom recombination event. Energetic considerations lend favor to the second route, though further experiments must be done to prove this. At temperatures above about 700K a parallel reaction route was evident. This route was believed to be due to reaction at step sites.

High Resolution Electron Energy Loss Spectroscopy Studies of Water Interaction with Ag(110) with Adsorbed Oxygen

E. Stuve

B. Sexton (G.M. Research Laboratories, Warren, Mich.)

The adsorption and reaction of water on clean and oxygen covered Ag(110) surfaces has been studied with high resolution electron energy loss (EELS), thermal desorption (TDS), and X-ray photoelectron (XPS) spectroscopies. Non-dissociative adsorption of water is observed on both surfaces at 100K. The vibrational spectra of these adsorbates at 100K compare favorably to infrared adsorption spectra of ice Ih. Both surfaces exhibit three desorption states which represent desorption of multilayer ice at 180K and monolayer H₂O desorption from hydrogen bonded and non-hydrogen bonded adsorbates at 200K and 240K, respectively. EEL spectra of the 240K state show librations among the adsorbed H₂O molecules which are assigned to restricted rotations of the molecule against ridge atoms of the (110) surface. A fourth desorption state is observed at 320K subsequent to exposure of the oxygen-dosed surface to water. The reaction of adsorbed H₂O with preadsorbed oxygen to produce adsorbed hydroxyl groups has been observed by EELS in the temperature range 205K to 255K. The adsorbed hydroxyl groups recombine at 320K to yield H₂O gas and adsorbed atomic oxygen. TDS and XPS results indicate that the water dissociation reaction goes to complete consumption of preadsorbed oxygen. A reaction mechanism which involves a solvation reaction between hydrogen bonded H₂O molecules and hydroxyl groups is proposed. This mechanism is shown to be consistent with results of this work and earlier work showing complete isotopic exchange between H₂¹⁶O_(a) and 18O_(a).

The Adsorption and Reaction of SO₂ with Clean and Preoxidized Ag(110).

D. Outka

Previous studies of reactions of adsorbed oxygen with CO, CO₂ and HCOOCH₃ have shown that the oxygen adatoms react readily to form CO₂, CO_{3(a)} and HCOO_(a) respectively. The adsorption and reaction of SO₂ with clean and oxygen covered Ag(110) was studied to further

extend our understanding of such reactions. SO_2 chemisorbed on the clean surface to produce states with desorption energies of 11.7 and 9.5 kcal/gmol at coverages corresponding to 0.5 and 0.75 monolayer respectively; $p(1 \times 2)$ and $c(4 \times 2)$ LEED patterns were observed. Pre-adsorbed oxygen reacted quantitatively with SO_2 to form adsorbed SO_4 species, as shown by XPS. This species decomposed with heating at 540K to yield SO_2 plus adsorbed sulfur and oxygen. UPS data are in reasonable agreement with those of LiSO_4 . These results indicate that clean silver is passive to attack by SO_2 , and the presence of adsorbed oxygen is required for corrosive behavior.

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35. ELECTROCATALYTIC OXIDATION OF GASEOUS
HYDROCARBONS ON SOLID-OXIDE ELECTROLYTES

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Agency Support: ACS-PRF-9864-AC7
DOE 10492

Technical Objective:

The goal of this research program is to obtain electrocatalytic data which will allow kinetics mechanisms to be established for selected hydrocarbons being oxidized on solid oxygen-ion type electrolyte anodes. A fundamental understanding of the kinetics of the electrode-electrolyte process is not only of scientific interest, but provides basic information useful in the design of such devices as fuel cells and oxygen sensors. Experimentation to date has shown the general reactivity of common fuel species: H_2 , CH_3OH , CO , C_2H_5OH and CH_4 with the reactivity in descending order. The most important experimental result is that the electrolyte surface contains the active catalytic sites--not the porous electrode--be it Pt, Au, or non-noble metal. These sites are hypothesized to be colored-centers (trapped electrons) or holes and in continuing work emphasis is being placed on experiments such as employing radiation to test this hypothesis. Steady-state and transient measurements varying temperature reactant concentrations, and surface morphology are being obtained to elucidate the mechanisms.

Research Report:

The anodic current-overpotential behavior of various pure gases at 1 atm and 700-850 C was investigated in a fuel cell system using an 8 mol % Sc_2O_3 -stabilized ZrO_2 disc electrolyte. Purified air was used

as a source of O_2 at the cathode, while the individual fuel gases reacted at the anode were: H_2 , CO , CH_3OH , C_2H_5OH and CH_4 . The working and reference cathodic and anodic electrodes comprised either porous Pt or Au. Low current-overpotential measurements were used to obtain exchange currents as a function of temperature, permitting values of activation enthalpy of the anodic electrocatalytic process to be calculated, which for a given gas (except CH_4) was found to be within 3 Kcal/mole for either Pt or Au electrodes. Activation enthalpies ranged from 20 - 30 Kcal/mole for the gases studied. This independence of the values of activation enthalpies on the electrode material for a given gas strongly suggests that the electrolyte and not the electrode metal is playing the major electrocatalytic role, since Pt and Au (or their compounds with Zr) would be expected to behave catalytically quite differently. High current overpotential measurements were made, with the electrolyte in two conditions: (1) a normal, unblackened state, and (2) a highly catalytic blackened state obtained by a specific current treatment. Anodic currents obtained using the blackened electrolyte were one to two orders of magnitude larger than those for the unblackened electrolyte. In both cases the fuel cell showed similar hydrocarbon reactivity at a given overpotential whether porous Pt or Au electrodes were used. This behavior together with the similarity in activation enthalpies observed for both Pt and Au supports the importance of the role the electrolyte surface plays, compared to the electrode, in the electrocatalytic process. It is hypothesized that the high reactivity of the surface of the electrolyte is due to the presence of electrochemically active F- or F'-centers the population of which is increased in the blackened state.

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36. PHYSICAL CHEMISTRY OF LIPID, LIPID-PROTEIN OR LIPID-DETERGENT
BILAYER MEMBRANES

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Agency Support:

NSF PCM 77-23586
NIH 2R01 AI13587
NSF PCM 8021993
NIH 5R01 AI13587

Technical Objective:

The aim of this research is to attain a more thorough understanding of the structure and function of biological and synthetic membranes.

Approach:

Various physical chemical techniques such as electron spin resonance (ESR), freeze-fracture electron microscopy, fluorescence recovery after photobleaching (FRAP), and two-dimensional gel electrophoresis are used to study the physical nature and chemical composition of biological and synthetic membranes.

Research Report:

(1) Investigation of Cytotoxic T Lymphocyte-Target Cell Interactions

Professional Associate: A. A. Brian

Lipid vesicles containing purified H-2 antigens elicit the proliferation of cytotoxic T lymphocytes (CTL) in vitro. At this time I am developing stable, clonal lines of CTL to provide homogeneous, highly specific cells for biophysical investigation of their interaction with targets containing purified antigens and biochemical characterization of receptor proteins.

(2) Development of a Technique that Facilitates in situ Electrophoresis of Membrane Components

Professional Associate: D. S. Cafiso

An elegant technique has been developed which facilitates the in situ electrophoresis of membrane components. The electrophoresis of integral membrane proteins, antibodies and lipids has been easily accomplished on planar bilayer systems with fields produced by a charged, microscopic, photochemically machined grid. The geometry of this system permits the accurate quantitation of changes in the concentration of labeled membrane components as monitored by epifluorescence microscopy. Several experiments are being carried out using this technique. We are studying the electrophoretic and electroosmotic properties of membrane components and plan to examine specific intramolecular associations between cell membrane components (e.g. cell surface antigens). In addition, this approach provides a powerful method for producing concentration profiles of membrane components of varied magnitude and geometry in a model membrane system. Such a model system may provide a versatile target membrane with which to study the immune system.

(3) Lateral Diffusion of Membrane Lipids and Antibodies Bound to Lipid Haptens in Model Membranes is Reduced in the Presence of Serum Albumin

Professional Associate: D. G. Hafeman

Serum albumin, at concentrations typically used in physiological cell media, binds to the surfaces of phospholipid monolayers and bilayers, and significantly reduces the lateral diffusion of a fluorescent lipid probe, and fluorescent antibodies specifically bound to lipid haptens. Diffusion coefficients can be reduced by factors ranging between ten and one hundred, depending on the physical state of the lipid and the concentration of serum albumin. It is likely that serum proteins also affect the lateral diffusion of some components of the plasma membranes of cells.

(4) Mechanism of Triggering of the Neutrophil Respiratory Burst

Professional Associate: D. G. Hafeman

Activation of neutrophils triggers a respiratory burst that depletes intracellular NAD(P)H. We have analysed the distribution of NAD(P)H fluorescence among human neutrophils by flow cytometry to determine if individual neutrophils activate by an all-or-none or by a continuous mechanism. Two distinct populations are observed. Activation with 12-O-tetradecanoyl phorbol-13-acetate causes a decline in the number of highly fluorescent cells and a corresponding increase in the number of weakly fluorescent cells. Increasing concentrations of the activator causes increasing numbers of cells to shift from the highly fluorescent population to the weakly fluorescent population. Cells with intermediate fluorescence are not observed. Thus neutrophils are triggered in an all-or-none fashion, indicating that at least one critical or highly cooperative process is responsible for neutrophil activation.

(5) Specific Antibody-Dependent Interactions Between Macrophages and Lipid Haptens in Planar Lipid Monolayers

Professional Associate: D. G. Hafeman

The binding of guinea pig peritoneal macrophages to planar lipid monolayers on alkylated glass requires lipid hapten in the monolayer, and specific anti-hapten IgG antibody. This is true for both "fluid" and "solid" monolayer membranes, where the lateral diffusion coeffi-

cients of both fluorescent lipid probes and bound fluorescent antibodies differ by at least two orders of magnitude between fluid and solid membranes. The region of the (macrophage membrane)-(monolayer membrane) contact can be readily observed using an epifluorescence microscope and fluoresceinated IgG antibodies, or fluorescent lipids. The fluorescence intensity of IgG antibodies bound to lipid haptens in fluid monolayer membranes in the region of the (macrophage membrane)-(monolayer membrane) contact is significantly enhanced in the early stages of binding (first 10 min at 24°C), due to a diffusive flux of the fluorescent antibodies into the region of membrane-membrane contact. Macrophage activation takes place immediately during a 10-min warm-up to 37°C and can be recognized by rapid, symmetrical cell spreading, the formation of "black holes" around the cells (probably due to superoxide facilitated photochemical bleaching of the fluorophore) and the release of the lysosomal enzyme cathepsin B. Specific antibody-dependent $1\text{-}^{14}\text{C}$ -glucose oxidation by these macrophages on fluid and solid monolayers is quite similar to that reported previously for fluid and solid bilayer vesicle target membranes. These results are significant for understanding the molecular interactions between membranes that are necessary for a macrophage cytotoxic response.

(6) A Rapid Method for the Purification of Membranes from Cell Suspensions and Tissues

Professional Associate: S. Q. Mehdi

Methods currently used for the preparation of membranes from cells and tissues require rigorous methods for cell and tissue disruption followed by complex centrifugation procedures. The methods are time consuming and the yield of pure membrane fractions is poor. We have developed a simple technique for membrane purification involving homogenization of cells and tissues followed by a single-step sucrose density gradient centrifugation for 1 hr at $96,000 \times g$. The yield of membranes (per gram weight of tissue or cells) is 5-10 times greater than those obtained by current methods. Immunologically these membranes are as good or better than those obtained by other methods. Membrane

marker enzymes and hormone receptors are also comparable.

(7) A Solid State Assay for Antibodies to Cell Surface Antigens

Professional Associate: S. Q. Mehdi

Graduate Student: F. D. Howard IV

Membranes prepared as described above stick firmly to plastic microtiter plates, under appropriate ionic conditions, in the presence of Ca^{++} . This enabled the development of an assay for cell surface antigens (histocompatibility antigens, hormone receptors, etc.), circumventing the need of using whole cells. Membranes prepared from cells can be kept frozen until needed. The sensitivity and specificity of the assay is better than that with whole cells.

(8) Fusion of Cell Surface Receptors onto a Foreign Cell - Physiological Response of the Live Recipient Cell to the Fused Receptor

Professional Associate: S. Q. Mehdi

Hormone receptors and histocompatibility antigens (cell membranes) are fused to foreign living cells not possessing them. Using thyroid membranes for fusion, TSH was found to stimulate adenylate cyclase activity in the recipient cell for 3-4 hrs following fusion. Similarly, cells that could not be killed by sensitized T-lymphocytes became susceptible to T-cell attack following fusion of the appropriate histocompatibility antigen.

(9) Structure and Function of Phagocytic Membranes

Professional Associate: H. R. Petty

We have studied the lateral distribution, diffusion, and capping behavior of cell surface molecules including HLA antigens, DR antigens, and C3b receptors using immunofluorescence and FRAPP techniques. We have examined the flow of cell surface area during phagocytosis with special reference to quantitation of the disappearance of macrophage surface folds. Accompanying these morphologic alterations of the plasma membrane, we have observed specific changes in cell surface protein composition using two-dimensional gel electrophoresis.

Following interaction at the plasma membrane, the target particle is internalized within a phagosome which is then degraded by lysosomal enzymes. We have been examining the conditions necessary for this interaction with ultrastructural cytochemistry.

(10) Study of Plasma Membrane Events Preceding Basophil Degranulation

Graduate Student: K. Balakrishnan

Dinitrophenylated lipid haptens in liposomes have been shown to trigger the release of serotonin from rat basophil leukemia (RBL) cells in the presence of specific anti-Dnp IgE. The physico-chemical properties of these synthetic target membranes can be varied at will by changing their composition, and one can study how that affects the level of firing by these basophils. Studying the interactions between basophils and these synthetic membrane targets may lead to a better understanding of the events that take place at the plasma membrane of the basophil preceding degranulation. This may lead to certain generalizations about other plasma-membrane mediated events, e.g. signal transduction from the outside to the inside of a cell during hormonal regulation of cellular activity.

(11) Study of Cell-Cell Recognition Phenomenon of H-2 Restriction

Graduate Student: G. C. Cartwright

My research over the last year has dealt with the cell-cell recognition phenomenon of H-2 restriction. This recognition event is mediated by two membrane proteins: a viral protein and a histocompatibility protein. I have purified both the vesicular stomatitis virus G protein and the H-2K^k protein. I have shown that these proteins can be reconstituted into large synthetic liposomes and be recognized by cytotoxic T cells, thus reproducing the original biological response. I have fluorescently-labelled both proteins, reconstituted them and shown that this system is also antigenically active. I am now using the technique of fluorescence recovery after photobleaching to attempt to determine if the two purified proteins are "associated" in the plane of the synthetic membrane. This experiment will allow me to

differentiate among three prospective molecular models for the phenomenon of H-2 restriction.

(12) Isolation of Cytotoxic T Lymphocytes

Graduate Student: T. E. Frey

My research has involved the isolation of an enriched population of virus specific, H-2 restricted cytotoxic T lymphocytes. The eventual aim is to explore the mechanisms of H-2 restriction and cell-mediated cytotoxicity at the molecular level.

(13) H-2 Cell Surface Motion in Virally-Infected Cells

Graduate Student: F. D. Howard IV

Cell surface motion is an important parameter in cell-cell interaction in the immune system. We are currently exploring the effect of viral infection on the major histocompatibility molecule's lateral mobility on a variety of cell types. Initial results point to a dramatic decrease in lateral mobility as a result of viral infection.

(14) Measurement of Rotational Motion in Membranes

Graduate Student: L. M. Smith

R. M. Weis

In the past year Robert Weis and myself developed a photobleaching method for the measurement of rotational motion of membrane components. This has opened up a previously inaccessible time scale for the measurement of membrane dynamics. Model systems for the study of cell-cell interactions are being developed.

(15) Studies of Phase Behavior and Diffusive Properties of Membranes

Graduate Student: R. M. Weis

Studies are being conducted on the phase behavior and diffusive properties of artificial lipid membranes, through the use of fluorescence photobleaching recovery techniques. This has been used to study translational and rotational motion of a fluorescent lipid analogue.

Membrane protein properties and lipid-protein interactions are studied. Currently the effect of bovine serum albumin binding to lipid diffusion in lipid monolayers is under investigation.

Reference Publications:

1. "Lateral distribution and diffusion of the C3b receptor of complement, HLA antigens and lipid probes in peripheral blood leukocytes," H. R. Petty, L. M. Smith, D. T. Fearon and H. M. McConnell, Proc. Natl. Acad. Sci. USA 77, 6587-6591 (1980).
2. "Disappearance of macrophage surface folds following antibody-dependent phagocytosis," H. R. Petty, D. G. Hafeman and H. M. McConnell, J. Cell Biol. 89, 223-229 (1981).
3. "An alternative view of phospholipid phase equilibria at the air-water interface - microscope and film balance studies," V. von Tscharner and H. M. McConnell, Biophys. J., in press.
4. "Phase equilibria in binary mixtures of phosphatidylcholine and cholesterol," D. J. Recktenwald and H. M. McConnell, Biochemistry, in press.
5. "Measurement of rotational motion in membranes using fluorescence recovery after photobleaching," L. M. Smith, R. M. Weis and H. M. McConnell, Biophys. J., in press.
7. "Phase equilibria in binary mixtures of dimyristoylphosphatidylcholine and cardiolipin," T. Berclaz and H. M. McConnell, Biochemistry, in press.
8. "Specific antibody-dependent interactions between macrophages and lipid haptens in planar lipid monolayers," D. G. Hafeman, V. von Tscharner and H. M. McConnell, Proc. Natl. Acad. Sci. USA, in press.
9. "Mobile haptens in liposomes stimulate serotonin release by rat basophil leukemia cells in the presence of specific IgG," K. Balakrishnan, A. D. Cooper and H. M. McConnell, J. Biol. Chem., in press.

37. DEFORMATION AND FRACTURE IN STRUCTURAL MATERIALS

Alan K. Miller, Associate Professor, Materials Science and Engineering

Professional Associates:

K. S. Chan

Graduate Students:

G. Henshall

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*Received Ph.D. during report period.

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Research Report:

(1) Modelling of Deformation and Fracture in High-Temperature
Structural Materials (with Professor Oleg D. Sherby)

The general objective of this research project is the development of improved quantitative methods for predicting deformation and fracture of metals and alloys under the complex histories and environments which are typical of energy-related systems. This work is intended to bring a greater physical content to the methods used by high-temperature designers. At the same time, the research aims to extend the applicability of our scientific understanding of deformation and fracture processes to more complex technologically-important situations. Thus to a certain extent this project serves as a bridge between the materials research community in mechanical behavior and the high-temperature structural design and analysis community.

In pursuing this objective, our basic mode of operation is the development of mathematical models which take advantage of relatively recent scientific understanding of the influence of microstructure on both deformation and fracture properties, but which also are sufficiently

general and quantitative to be relevant to real-world predictions. In the area of modelling of non-elastic deformation, such models are termed "unified constitutive equations based on internal (or state) variables" and are increasingly cited as a key need in finite-element analyses of both structures and metal forming operations. In the area of modelling of fracture, no common terminology has yet emerged but clearly similar needs are present, i.e. the need to incorporate our scientific understanding of crack nucleation and growth processes, the need to be general enough to handle complex problems such as fracture under variable-amplitude loadings, and the need to be fully quantitative in predicting failure and the effects of material variables such as initial defect sizes.

Our work in modelling non-elastic deformation has focussed on the "MATMOD" constitutive equations and, indeed, this research contract has now become the center of activity for improvements in this model, which is increasingly being utilized by industry. The physical basis of the "MATMOD" equations lies in the fact that they contain structure variables which represent three distinct categories of strengthening mechanisms: (1) solute strengthening (and other mechanisms which do not depend on work hardening), (2) isotropic work hardening (such as subgrain and forest dislocation strengthening), and (3) directional work hardening (such as due to dislocation pileups). The role of each variable in the equations parallels the role of the corresponding physical variable in real materials, and the auxiliary equations which govern changes in each variable also parallel our understanding of the microstructural changes which occur during non-elastic deformation. Thus, for example, the structure variable which represents solute strengthening (F_{sol}) depends on the non-elastic strain rate and temperature in the same manner that the solute atmosphere drag force on dislocations is thought to vary with the dislocation velocity and solute diffusivity.

Clearly advances are also needed in the state of understanding of the physical processes in these three categories, thus an important aspect of this contract are projects to study individual strengthening mechanisms in greater detail and/or greater generality. Our

experimental work on transient hardening due to subgrains and forest dislocations fits this category.

The modelling of deformation connects with the modelling of fracture in a number of ways, some obvious, some more subtle. At the obvious level, deformation response determines the macroscopic stress amplitude and plastic strain range under particular loadings as well as the local behavior at the tips of cracks. It also determines the rate of work hardening and the strain rate sensitivity, both of which are important in predicting ductile rupture. Detailed tracking of the relative contributions of grain matrix deformation and grain boundary sliding can help predict intergranular fracture under creep-fatigue conditions. Considerations of solute redistribution and oxide cracking form the basis for an improved model for predicting elevated-temperature fatigue life with hold periods, in $2\frac{1}{2}$ Cr - 1 Mo steel, as shown in last year's report. Prediction of plastic flow concentration (sometimes associated with strain softening) is important in fatigue crack initiation. And, in the area of multiaxial deformation, the details of the yield locus are critical in determining sheet formability.

From among these numerous considerations, we have selected fatigue crack initiation and growth as an area for concentrated work. The objective is development of a unified, physical-phenomenological model for these processes, one which will be able to treat the full range of possible defect sizes ranging from essentially zero (as in many laboratory investigations on small specimens) to short cracks (which are known to behave differently from long cracks at equal stress intensity) to cracks in the linear elastic fracture mechanics regime. Such capability for predicting the effects of flaws of all sizes should thus connect logically to the physical processes which produce defects of various sizes, ranging from deformation bands within individual grains up to macroscopic welding flaws. In developing such a unified model for fatigue crack initiation and growth, we are not starting "from scratch", but are using as a point of departure the "SCCIG" [Stress Corrosion Crack Initiation and Growth] model developed for prediction of Zircaloy iodine-induced fracture in light-water

reactors, under EPRI sponsorship.

To accomplish the above objectives, a number of specific research tasks have been and are being conducted. Clearly the separate tasks interrelate strongly. Two of them are totally completed; these include (1) the development of an explanation and predictive model for the effects of hold periods on elevated temperature fatigue of $2\frac{1}{2}\text{Cr-1Mo}$ steel and (2) the development of an improved version of the MATMOD equations with respect to solute strengthening. An experimentally-oriented task on back stresses and their role in monotonic and cyclic deformation is near completion, but some of the data are undergoing continued analysis with respect to strain softening. An experimental task on the separate roles of subgrains and forest dislocations in isotropic hardening has provided the clear, but controversial, conclusion that forest dislocations dominate work hardening in type 304 stainless steel even when subgrains are also present. We are presently applying the same experimental techniques to other alloys to see if the above conclusion is general, or specific only to low stacking fault energy materials like 304 stainless steel. An analytical task entitled "strain softening" is currently the focus of a number of potential improvements in the MATMOD equations, involving not only strain softening behavior under complex histories but also multiaxial plastic flow behavior. (In this latter study, we have begun to interact with Dr. S.S. Hecker of Los Alamos Scientific Laboratory.)

Last, we have recently begun a major task on fatigue, to develop the unified, physical-phenomenological model for fatigue crack initiation and growth which was mentioned above. Thus far it appears that the computationally-efficient method by which the local stress and strain distributions are computed in the "SCCIG" model is also suitable for this new fatigue model. Appropriate local failure criteria such as the maximum local plastic strain energy (for "Stage I" fatigue cracking) and peak tensile stress (for "Stage II" fatigue cracking) are being developed, as are modifications to deal with crack closure, cyclic hardening, and other effects peculiar to the fatigue situation. While for the present we are concentrating on regimes of

fatigue fracture where strain rate and environmental effects are not significant, eventually we hope to be able to incorporate these (in a physically-meaningful manner) by drawing on the MATMOD and SCCIG models, respectively.

(2) Zircaloy Cladding Deformation and Fracture Analysis

Technical Objective:

To develop a physically-based model for the stress-corrosion-cracking (SCC) fracture of Zircaloy nuclear fuel cladding due to pellet-clad interaction (PCI).

Approach:

The model developed is required as part of a larger EPRI code development project which seeks to predict the durability of light-water nuclear reactor fuel under transient power conditions. The researchers at Stanford University have had the responsibility for developing an appropriate SCC fracture model, utilizing experimental data generated mostly by other participants in the overall project. Therefore our approach has been mainly to conduct physically-based analyses of the outside data, to develop mechanistic interpretations of the material's behavior, and to distill the results of these analyses into a useable mathematical framework.

Results:

To predict the response of Zircaloy tubing in iodine environments under conditions where either crack initiation or crack propagation predominates, a unified model of the SCC process has been developed based on the local conditions (the local stress, local strain, and local iodine concentration) within a small volume of material at the cladding inner surface or the crack tip. The methodology used permits computation of these values from simple equations. A nonuniform distribution of local stress and strain results once a crack has initiated. The local stress can be increased due to plastic constraint and triaxiality at the crack tip. Iodine penetration is assumed to be a surface diffusion-controlled process. Experimental

data are used to derive criterial for intergranular failure, transgranular failure, and ductile rupture in terms of the local conditions. The same failure criteria are used for both crack initiation and crack propagation. Irradiation effects are included in the model by changing the value of constants in the equation governing iodine penetration and by changing the values used to represent the mechanical properties of the Zircaloy.

Variability is treated in a physically-meaningful manner through the use of a probabalistic distribution of flaw sizes representing both chemical and mechanical defects. The unified nature of the model permits it to treat the full range of possible flaw sizes from zero up to the linear elastic fracture mechanics (LEFM) regime.

Model simulations of time-to-failure vs. average hoop stress and temperature (for initially smooth specimens of irradiated Zircaloy) agree well with data. Simulations involving various initial crack sizes show that for long cracks the crack growth rate dc/dt depends solely on the stress intensity K , but that for short cracks dc/dt is not a unique function of K . The model is applicable to complex-history situations where cumulative damage behavior is important; for example, good agreement is obtained between data and independent predictions of cumulative-damage stress-change tests on irradiated cladding. The model readily permits predictions of failure in experiments in which specimens initially held at high stresses are later exposed to aggressive environments below the threshold value.

The approach taken enables one to predict the response of the large quantities of tubing typically exposed in-reactor. Such predictions were obtained by using the information relating flaw size to SCC response and an equation describing the flaw size distribution vs. the area of exposed cladding. The model predicts that the resistance of a fuel assembly to SCC (as measured by threshold stress and time-to-failure values) can be substantially less than that of a small number of laboratory speciemns. This approach permits one to explain the reproducible results obtained in laboratory experiments on small quantities of tubing and the strongly variable response

following in-reactor exposure of large quantities of tubing.

(3) Modelling of In-Reactor Deformation Behavior of Fast Breeder
Reactor Core Structural Materials

There has been a growing awareness of the need for physically based models to describe the in-reactor deformation of LMFBR core materials such as AISI 316. We have developed a preliminary approach for such a model based on the MATMOD constitutive equations developed at Stanford. Details of the approach address the major physical and mechanical processes important in deformation during irradiation. These include: (1) The description of the total strain rate as a function of thermal and irradiation components, (2) irradiation hardening and softening due to dislocations, Frank loops, voids and precipitates, (3) the effects of precipitation on swelling and irradiation creep, (4) the effects of temperature history, stress and flux on swelling, and (5) description of steady state irradiation creep rate as a function of temperature flux and stress.

The key conclusion at present can be summarized as follows:

- 1) The present MATMOD equations are capable of modeling the out-of-reactor deformation behavior of AISI 316. This includes thermal strain rate, creep properties and complex temperature, stress and strain rate histories.
- 2) The framework for a derivative model to describe in-reactor deformation has been developed. Important state variables have been identified and general equations outlined. The model is built around the equation for the total non-elastic strain rate $\dot{\epsilon}$:

$$\dot{\epsilon} = \dot{\epsilon}_{\text{thermal}} + \dot{\epsilon}_{\text{irradiation}} \quad (1)$$

- 3) The thermal component of the strain rate will be modeled through the structure variables F_{def} and $F_{\text{sol},1}$. These parameters are described by the equations:

$$\dot{F}_{\text{def}} = \frac{dF_{\text{def}}}{dt} = H|\dot{\epsilon}| + [K - f(F_{\text{def}})]\dot{\epsilon} - f(T, F_{\text{def}}) \quad (2)$$

$$\dot{F}_{sol,1} = \frac{dF_{sol,1}}{dt} = f(T, \dot{\epsilon}, \phi, F_{sol,1}) \quad (3)$$

4) The approach presented here for modelling the thermal component of the strain rate has several advantages, including: (1) Reduction to out-of-reactor behavior when $\phi = 0$, (2) modelling of irradiation hardening and softening, (3) modeling of the saturation of strength and microstructure, (4) independence of final irradiated structure and properties on initial conditions, and (5) temperature dependence of final irradiated structure and strength properties.

5) Radiation induced microchemical evolution is treated as a problem involving changes in the thermodynamic driving force and kinetics of precipitation. The general format for such a treatment is given below using the relation for the thermodynamic and kinetic portions, respectively:

$$\dot{C}_{Ni} = R \cdot f(T, \phi, C_{Ni}) \quad (4)$$

$$R = A \exp \left[\frac{-(Q_0)}{kT} \right] \quad (5)$$

6) The state variables for swelling have been identified and are expressed in the form:

$$\dot{V} = f(T, C_{Ni}, \sigma_H, V)\phi \quad (6)$$

This allows for modeling of temperature and temperature history effects, stress enhancement, and effects of microchemistry.

7) A simplified approach which describes irradiation creep in terms of the steady-state behavior was presented. The approach centers around the equation:

$$\dot{\epsilon}_{ss,irr creep} = f(T, C_{Ni})\sigma\phi \quad (7)$$

together with equation (4).

Publications since June 1980

1. K.D. Challenger, A.K. Miller and R.C. Brinkman, "An Explanation for the Effects of Hold Periods on the Elevated Temperature Fatigue Behavior of 2½Cr-1Mo Steel", J. Engg. Mat. and Tech., 103, 7-14, 1981.
2. K.D. Challenger and A.K. Miller, "Elevated Temperature Fatigue with Hold Time in a Low Alloy Steel: A Predictive Correlation" J. Materials for Energy Systems, in Press 1981.
3. C.G. Schmidt and A.K. Miller, "A Unified Phenomenological Model for Non-Elastic Deformation of Type 316 Stainless Steel, Part I: Derivation of the Model", Res. Mechanica, in Press, (1981).
4. C.G. Schmidt and A.K. Miller, "A Unified Phenomenological Model for Non-Elastic Deformation of type 316 Stainless Steel, Part II: Fitting and Predictive Capabilities", Res. Mechanica, in Press, (1981).
5. A.K. Miller and A.A. Ziaai-Moayyed, "Some Critical Experimental Tests of the MATMOD Equations with Respect to Directional Hardening and Cyclic Deformation" ASTM Symposium on Mechanical Testing for Deformation Model Development, Bal Harbour, Fla., Nov. 1980 (To be published in ASTM STP).
6. A.K. Miller, H. Ocken and A. Tasooji, "Iodine Stress Corrosion Cracking of Zircaloy: Laboratory Data, a Phenomenological Model, and Predictions of In-Reactor Behavior" J. Nuclear Materials, in Press 1981.

38. MULTIAXIAL FATIGUE

D. V. Nelson, Assistant Professor, Mechanical Engineering

Graduate Student:

S. Tipton

Agency Support:

NSF CME 8006692
Deere & Co. Technical Center

Technical Objective:

Many structures and mechanical components experience multiaxial cyclic straining and resulting fatigue damage. In most cases, the straining is non-proportional (i.e., principal strains vary in ratio and/or directions). The objectives of this research are: (a) to improve the understanding of multiaxial fatigue behavior and (b) to develop methods for predicting fatigue life, suitable for use in computer-aided design evaluations.

Approach:

Methods for predicting the life to formation of fatigue cracks and their subsequent growth rate in components which experience uniaxial fatigue are fairly well-established. However, due to the experimental and analytical complexities of the subject, comparably adequate methods for multiaxial fatigue have yet to be developed. In order to help close the gap between the respective states of knowledge in uniaxial and multiaxial fatigue, a cooperative university-industry research program has been established to study the fatigue behavior of a specimen with a stress concentration (notch) subjected to a variety of complex multiaxial loadings. The bulk of testing will be conducted by industry, while most of the life prediction method development will be done at Stanford.

Research Report:

A multiaxial test system capable of applying constant amplitude combined bending and torsion, both in-phase and out-of-phase, as well as highly irregular bending and torsion characteristic of actual service loadings, has been designed, fabricated and checked out. The system is controlled by a mini-computer and data on the applied loadings and cyclic multiaxial straining are monitored, stored and processed by the computer. At present, five industrial research labs (three U.S. and two European) plan to contribute testing to the project and will duplicate the test system developed under this program. The formation of cracks in the fatigue specimens is detected with a surface acoustic wave transducer. Their growth is being tracked with a new magnetic particle surface replica technique until they reach a size large enough to be monitored by conventional optical means.

The test specimen is a large round bar with a fillet (notch). Preliminary tests indicate that analytical methods commonly used for predicting notch cyclic plastic straining (e.g., Neuber's rule) significantly overestimate strains for the specimen/notch configuration being studied. It is also already evident that most of the total fatigue is spent in crack growth for the metal (1045 steel, 200 BHN) and multiaxial test conditions currently being investigated.

The use of computed multiaxial cyclic plastic work as a general method for predicting the life to crack formation is being evaluated. This approach, which requires as input only the more easily generated uniaxial fatigue and cyclic stress-strain properties, could be readily adapted for use in design analysis.

Reference Publications:

1. Nelson, D.V. and Socie, D.F., "Crack Initiation and Propagation Approaches to Fatigue Design," submitted to Design of Fatigue and Fracture Resistant Structures, ASTM.

39. RELATIONS BETWEEN CRYSTALLINE IMPERFECTIONS AND THE PHYSICAL PROPERTIES
OF CRYSTALS

William D. Nix, Professor, Materials Science and Engineering

Professional Associates:

J. C. Gibeling
T. H. Alden
W. Blum
L. Martinez
J. S. Wang

Graduate Students:

K. P. Fuchs	M. J. Mills
J. C. Earthman	W. C. Oliver*
J. K. Gregory	J. D. Smith
D. A. Hughes	J. J. Stephens
	J. C. Wei*
	J. L. Yuen

*Received Ph.D. during report period

Agency Support

AFSOR 81-0022
DOE DR ATO3-79-ER103 78
NSF-MRL Through CMR
NSF DMR 79-23942

Technical Objective:

To understand and exploit the relation between imperfections and the physical properties of crystalline solids. To develop techniques for predicting and controlling the mechanical and electronic behavior of crystalline materials in order to establish guidelines for making both structural and electronic materials.

Approach:

To carry out both theoretical and experimental investigations of crystalline solids with known concentrations of various types of defects.

Research Report:

(1) Theoretical Study of High Temperature Fracture

Research Associate: L. Martinez

Many structural materials subjected to high temperature creep fail by the growth and coalescence of cavities at the grain boundaries. Diffusion controlled mechanisms have been proposed wherein the growth results from atomic transport of material away from the cavity, mainly along the cavity surface and through the adjoining grain boundary. The models can be divided in two categories: those considering that the diffusion process is controlled at the grain boundary, $d_b \ll D_s$ (Hull and Rimmer, Speight and Harris, Raj and Ashby) and at the cavity surface, $D_s \ll D_b$, (Chuang and Rice, Pharr and Nix, Fuentes-Samaniego and Nix). In order to explore the wide region between these two limiting cases, we developed a numerical model to simulate the time dependent diffusive cavity growth for different grain boundary to cavity surface diffusivity ratios ($0.5 \leq D_b \delta_b / D_s \delta_s \leq 10^4$). The results we obtain confirm that the cavity tip grows like a crack of the model of Chuang and Rice and that the power law for growth predicted by them is essentially correct.

(2) A Study of the Mechanisms and Mechanics of Creep Crack Growth in Metals at High Temperatures

Research Associate: J. C. Gibeling

Research Student: J. C. Earthman

Although creep and creep fracture are important deformation and fracture processes at high temperatures, actual failure usually occurs by the initiation and growth of cracks. The prediction of failure requires not only some knowledge of the microscopic mechanisms of decohesion (fracture), but also some understanding of the mechanics of cracks. Our research is aimed at extending our understanding of the microscopic mechanisms of intergranular fracture to the study of cracked samples which are tested under creep conditions. Our experiments with Ag, Cu and Ni containing water vapor bubbles and dispersions of stable

second phase particles clearly demonstrate that we can control the matrix strength, grain boundary properties and fracture mechanisms in these materials. Our goal is to study creep crack growth for various material conditions to determine whether deformation or fracture dominate the crack growth process.

(3) Applications of Stress Change Experiments to the Study of High Temperature Creep

Graduate Students: M. J. Mills

A new technique for determining the internal stresses in creeping solids has been developed recently by Blum. This technique is based on measurements of the total negative creep strain following stress reductions. We are currently measuring internal stresses in aluminum using this method. This new approach promises to yield internal stresses which are relatively independent of the time resolution of the measuring system.

A new high resolution creep apparatus has been built for the above experiments. This new equipment will be used for the study of anomalous creep effects following large stress reductions during creep.

(4) Elongated Grain Formation in Oxide Dispersion Strengthened Nickel Alloys

Graduate Student: J. K. Gregory (jointly with Professor R. Sinclair)

One beneficial and peculiar aspect of oxide dispersion strengthened alloys involves the microstructure. Annealing above some critical temperature causes grains of submicron size in an as-extruded sample to grow anisotropically. For ODS nickel superalloys, this temperature is related to the amount of deformation, and thus the energy contained within the structure. Below this temperature, only grain coarsening occurs, inhibiting elongated grain formation.

For this study, Transmission Electron Microscopy will be used to examine Inconel Alloy MA 6000E and MA 753 to answer the following questions: 1) What is responsible for the anisotropy of the grain growth ?

And, 2) What is the process which is triggered at high temperatures and inhibited at lower temperatures ? 3) What is the critical amount of deformation needed in these materials ?

(5) Diffusional Creep of Dispersion-Strengthened Alloys

Graduate Student: J. J. Stephens

We are studying diffusional creep of the dispersion-strengthened Ni-base alloy Ma-754 at temperatures near $.95 T_m$. We are especially interested in the formation of particle free zones near grain boundaries during diffusional creep. We wish to determine the role of such particle free zones on creep and failure processes in ODS alloys. We are also interested in studying the effects of grain shape on the diffusional creep process and on the possible existence of a threshold stress for diffusional creep.

(6) The Shape Evolution of Intergranular Cavities in Copper During Creep

Professional Associates: L. Martinez

J. S. Wang

The evolution of the shape of intergranular cavities during diffusional cavity growth is being studied. The experimental observations in copper show that the initial rounded cavities in grain boundaries develop "noses" at their tips. A technique was developed to introduce large and rounded cavities (4 to 6 μm in diameter) into the grain boundaries of OFHC-copper. This method consists of pre-straining the sample by creep well into the secondary creep stage. Then the sample is partially unloaded to reduce the applied stress to a minimum ($\approx .7$ MPa) to produce sintering of the smaller cavities. Also during this time the cavities larger than a critical size suffer a process of rounding and minimum growth. Finally the sample is creep treated at a lower temperature and at higher stresses (≈ 15 MPa) until fracture occurs. Both optical and SEM observations of the regions near the fracture surface show that the cavities develop "noses" at the tips. The calculations using a model for cavity growth show that these noses

can be explained if surface diffusion is considerably less than grain boundary diffusion.

(7) The Interaction of Dispersion Strengthened and Solute Strengthening in Al-Mg Alloys

Graduate Student: W. C. Oliver

The mechanical properties of dispersion strengthened (D.S.) Al and Al-3.9% Mg (IN-9051) have been studied. The purpose of the work is to better understand the interactions of dispersion strengthening and solute strengthening in metals.

The steady state creep behavior of these alloys have been studied using both constant crosshead speed compression tests and constant stress compression creep tests. The constant crosshead speed tests are performed on an Instron machine in conjunction with an H.P. 9825 data acquisition system.

The steady state creep properties of D.S. Al-3.9% Mg demonstrate several interesting characteristics. Above the apparent threshold stress the presence of particles weakens the matrix by eliminating solute drag as a rate controlling process. The addition of magnesium to D.S. aluminum causes the dispersoid to be made up of MgO rather than Al_2O_3 . This results in the reduced elevated temperature strength of D.S. Al-Mg when compared with D.S. Al. Calculations of the effect of particles on solute atmospheres around dislocations have been made. A model for deformation of O.D.S. alloys below the Orowan stress has been developed. Comparisons of the properties mechanically alloyed D.S. alloys with rapidly solidified powder alloys as well as other less expensive techniques for producing D.S. alloys are planned.

(8) The Influence of Mechanical Properties on the Behavior of Materials for Microelectronic Applications

Research Associate: J. C. Gibeling

It is readily apparent that advances in the miniaturization of electronic devices will continue to present interesting and important

fundamental materials problems. While the electronic properties of materials have a direct influence on device performance, other properties play equally important roles in reliability, fabrication and device lifetime. This category includes diffusivity, structural properties, transformation characteristics and mechanical properties. This program is based on the idea that microstructural concepts and techniques can be applied to the study of metals, insulators and semiconductors to solve fundamental materials problems associated with microelectronic devices. Our research involves a study of the influence of mechanical properties on the behavior of materials used in electronic applications.

(9) Studies of the Fracture Surfaces of Cu Alloys by Scanning Auger Spectroscopy

Graduate Student: K. S. Yu (Jointly with Professor Heinemann)

The presence of impurities such as antimony in copper have a significant effect on the mechanical properties. In addition to solid solution strengthening, such impurities produce an embrittlement effect as well. It is generally believed that the embrittlement effect is due to the impurity atoms that segregate at the grain boundaries in copper and consequently reduce the cohesive forces between the grains. Cu-Sb alloys crept almost to fracture in air and then placed into a high vacuum environment have been studied by scanning Auger spectroscopy in order to determine the nature of the segregation effect. A fracture stage to break the samples in-situ in a high vacuum chamber has been designed and installed to avoid contamination of the samples at the time of fracture and to obtain with more accuracy the depth profile of the solute concentration.

Reference Publications

1. R. F. Singer, W. Blum and W. D. Nix, "The Influence of Second Phase Particles on the Free Dislocation Density During Creep of Stainless Steel", Scripta Met. 14, 755 (1980).
2. R. Fuentes-Samaniego, W. D. Nix and G. M. Pound, "Vacancy and Substitutional Solute Distribution Around an Edge Dislocation

- in Equilibrium and in Steady-State Glide Motion", *Phil. Mag. A.*, 42, 591 (1980).
3. J. C. Gibeling and W. D. Nix, "A Numerical Study of Long Range Internal Stresses Associated with Subgrain Boundaries", *Acta Met.*, 28, 1743 (1980).
 4. R. F. Singer, W. C. Oliver and W. D. Nix, "Identification of Dispersoid Phases Created in Aluminum During Mechanical Alloying", *Metall. Trans.*, 11A, 1895 (1980).
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 10. T. G. Nieh and W. D. Nix, "Embrittlement of Copper due to Segregation of Oxygen to Grain Boundaries", *Metall. Trans.* 12A, 893 (1981).

40. PHOTON PRODUCTION FROM HIGH ENERGY ELECTRON BEAMS

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Professional Associate:

M. A. Piestrup

Graduate Students:

A. N. Chu*
J. A. Edidhoffer*
A.-M. Fauchet**
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**Received MS during report period.

Agency Support:

DE-AS03-76ER71042, P.A. 42
DE-AT03-78ER70064, P.A. 64
NSF ENG76-11244
ONR N00014-78-C-0403

Technical Objective:

To obtain sources of optical, x-ray and γ -ray radiation for materials research.

Approaches:

Three methods for the generation of electromagnetic radiation are being studied using relativistic electrons. Two methods, transition and channeling radiation, are designed to produce soft and hard x-rays. Transition radiators are being considered as possible sources for x-ray lithography, while channeling radiation in crystals is being considered as a method for analyzing defects in the crystals themselves.

We have also been studying a device we have termed the optical

klystron which will generate coherent infrared, visible and ultraviolet radiation. This device promises to have high gain and a broad tuning range; the latter property being important for spectroscopy. The optical klystron utilizes a high energy electron and laser beams to produce bunched electrons which are then allowed to reradiate with gain. Two major experimental breakthroughs occurred in the past year: the observation of coherent Cerenkov radiation and of momentum modulation of electrons using laser light.

Research Report:

- (1) Transition Radiation as a Source of X-ray Radiation (previously NSF-MRL supported research and seed program).

Relativistic charged particles crossing the boundary between two media with different dielectric constants produce x-rays by a process known as transition radiation. The photon yield is small for a single interface between two dielectrics; however, a summation from each of a large number of interfaces is possible, resulting in a large flux. A two orders of magnitude greater than synchrotron radiation is possible.

In the past year two sets of experiments have been performed. In one experiment, soft x-rays were observed from various targets using 90 MeV electrons.^(1,2) The radiators consisted of 1.0 μm foils of Al, 1.5 μm of mylar and 1.0 μm of Be. The photon flux for each radiator peaked at 1100, 1000, and 800 eV respectively. This was the first observation of such soft x-rays from transition radiation. Such radiation is well suited for x-ray lithography since it is brighter than conventional sources, collimated, and at the proper frequency for good film exposure.

A second experiment using the SLAC 4 GeV positron beam was performed. In this experiment coherent addition of the x-rays flux from individual foils was observed. Several resonance peaks were found in the 5 keV to 15 keV frequency range. Theoretical work is being done to see if such a phenomenon can be used to achieve stimulated x-ray emission.

Reference Publications:

- (1) A. N. Chu, M. A. Piestrup, T. W. Barbee, Jr., R. H. Pantell, and F. R. Buskirk, "Observation of Soft X-ray Transition Radiation from Medium Energy Electrons," Rev. Sci. Instrum. 51, 597 (1980).
- (2) A. N. Chu, M. A. Piestrup, R. H. Pantell, and F. R. Buskirk, "Soft X-ray Production from Transition Radiation Using Thin Foils," J. Appl. Phys. 52, 22 (1981).

(2) X-ray and γ -ray Emission from Channeled Electrons and Positrons

Relativistic electrons and positrons traverse periodic trajectories when channeled in a crystal lattice. This results in the emission of forward-directed electromagnetic radiation of relatively narrow line-width. For incident particles with energies in the range from 25 MeV to 60 MeV, the photon energies are in the range from 20 keV to 130 MeV.

Radiation from planar-channeled electrons and positrons has been observed, and the major spectral features are in agreement with calculations. In the past year, radiation from transitions between non-adjacent eigenstates (i.e. $\Delta n = 3$) of planar-channeled electrons has been measured, and the intensities are in reasonable agreement with theory.⁽⁵⁾

Most recently, electron channeling radiation has been observed from silicon crystals at elevated temperatures and from diamond crystals with defects. Although there is not presently any theory which can give qualitative results in these areas, the experiments are useful because they broaden the range of conditions under which channeling radiation has been observed, and contribute to better understanding of the phenomenon.

In addition to providing a potentially useful source of x- and γ -radiation for other applications, channeling radiation can be related to properties of the crystal itself, such as imperfections, bonding potentials, and impurities.

Reference Publications:

- (1) M. J. Alguard, R. L. Swent, R. H. Pantell, S. Datz, J. H. Barrett,

- B. L. Berman, and S. D. Bloom, "Radiation from Channeled Leptons," Nucl. Instrum. Meth. 170, 7 (1980).
- (2) R. L. Swent and R. H. Pantell, "A Model of Crystal Potential from Axial-Channeling Radiation," J. Appl. Phys. (volume and page numbers not yet available), (1981).
 - (3) R. H. Pantell, R. L. Swent, S. Datz, M. J. Alguard, B. L. Berman, and S. D. Bloom, "Characteristics and Applications of Channeling Radiation from Relativistic Electrons and Positrons," IEEE Trans. Nucl. Sci. NS-28, 1152 (1981).
 - (4) W. Zakowicz and R. H. Pantell, "Effects of Dislocations on Channeling," J. Appl. Phys. (volume and page numbers not yet available), (1981).
 - (5) B. L. Berman, S. D. Bloom, S. Datz, M. J. Alguard, R. L. Swent, and R. H. Pantell, "Observation of Radiation from $\Delta n = 3$ Transitions for Planar Channeled Electrons," Phys. Lett. A 82A, 459 (1981).
 - (6) R. H. Pantell, R. L. Swent, S. Datz, M. J. Alguard, B. L. Berman, and S. D. Bloom, "The Radiation Characteristics of Channeled Particles," Proc. SPIE Technical Symposium East '81 (volume and page numbers not yet available) (1981).

(3) The Optical Klystron

Two experiments have been performed which indicate that the optical klystron is possible. In the first experiment, light at $1.06 \mu\text{m}$ from a 30 MW Nd:YAG laser intersected 102 MeV electrons at an angle of 18 mrad in hydrogen gas which was used to phase match the electrons' velocity with that of the light's velocity in the gas. A significant change in the electrons' energy was measured indicating coherent velocity modulation, and possible coherent density variation in the electron beam.

In a second experiment, coherent Cerenkov radiation at the second harmonic of the laser frequency ($0.532 \mu\text{m}$) was measured and indicated the electrons were bunched on the order of the laser wavelength as a result of being velocity modulated by the laser.

An experiment is now being designed to enhance the coherent Cerenkov and to possibly achieve self sustained oscillation.

Reference Publications:

- (1) J. A. Edighoffer, W. D. Kimura, R. H. Pantell, M. A. Piestrup, and D. Y. Wang, "Observation of Inverse Cerenkov Interaction between Free Electrons and Laser Light," Phys. Rev. A 23A, 1848 (1981).
- (2) J. A. Edighoffer, W. D. Kimura, R. H. Pantell, M. A. Piestrup, and D. Y. Wang, "Free Electron Interactions with Light Using the Inverse Cerenkov Effect," submitted to IEEE J. Quant. Electr. (1981).
- (3) W. D. Kimura, D. Y. Wang, M. A. Piestrup, A. M. Fauchet, J. A. Edighoffer, and R. H. Pantell, "Observation of Coherent Cerenkov Radiation at Optical Frequencies," in preparation (1981).

41. PHYSICAL CHEMISTRY OF OXIDES AND OXIDE SURFACES

G.A. Parks, Professor, Applied Earth Sciences

Graduate Students:

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Demetrius Pohl (Geology Department)

Agency Support:

Stanford Institute for Energy Studies
School of Earth Sciences (McGee Fund)
Department of Applied Earth Sciences (Crook Fund)
NSF CPR-7920012

Technical Objectives:

1. Collection, through experiment and literature search, of intrinsic surface ionization constants and adsorption equilibrium constants needed for solute transport modelling. Contexts include radioactive waste disposal, mineral exploration, wastewater treatment and reinjection and solution mining.
2. Evaluation and experimental determination of the water solubility of UO_2 , and stability constants for formation of complexes of U(IV) under conditions ranging from 100 to 500°C and 1 to 1000 bars.

Research Reports:

(1) Intrinsic Adsorption Constants (Tripathi). The objective of the experimental work is to measure the equilibrium adsorption density of U(VI) onto goethite and to determine equilibrium constants for the adsorption process which can be used with the model SCMA (Davis et al, 1979). The objective also includes study of the effect of complexing ligands such as CO_3^{2-} , F^- and PO_4^{3-} on the sorption process.

Experimental Work. The majority of experiments completed to date have been performed in ligand-free systems. Careful attention was paid to design of experiments including establishing equilibrium time for adsorption, establishing losses due to sorption on the container walls, and establishing reversibility and reproducibility of sorption experi-

ments. Experimental work completed has demonstrated that in general, adsorption of U(VI) onto goethite, in ligand-free systems, is similar to adsorption of other divalent metals on oxide surfaces. Further experiments in ligand-free systems will be done to study the adsorption at very low ionic strength, very low dissolved uranium (2-20 ppb) and high uranium concentration (>400 ppb).

Preliminary experimental work has shown that dissolved carbonate inhibits adsorption of uranium in alkaline solutions ($\text{pH} > 8$). Detailed work will be performed under carefully controlled CO_2 atmosphere of varying CO_2 partial pressure. The effect of F^- and PO_4^{3-} will be studied in the pH range 5.9. Sigg and Stumm (1981) have noted the possibility of slow adsorption of PO_4^{3-} onto goethite surface, perhaps leading to the formation of Fe(III)-PO_4 solid. In our experiments care will be taken to avoid saturation with respect to Fe(III) or uranium (VI) solids (other than goethite).

Determination of Equilibrium Constants for U(VI) Adsorption.

The determination of intrinsic adsorption constants, from adsorption experiments, which can be used with SGMA depends on a knowledge of stability constants of U(VI) aquo complexes with OH^- and any other ligands present in solution (F^- , PO_4^{3-} , CO_3^{2-} in our experiments).

We have completed critical evaluation of thermodynamic literature and compilation of pertinent stability constants. Final calculations are awaiting acquisition of original data from some investigators for use in assessing one or two of the least reliable constants.

Development of a Transport Model. A chromatographic simulation model is being developed to study the effect of the adsorption process and its interaction with solution chemistry on partitioning of U(VI) between solution and the surface during transport in groundwater systems. All algorithmic development has been completed. FORTRAN coding of the program is in progress.

(2) Solubility of UO_2 (Pohl). The determination of the solubility of uranium (IV) dioxide and elevated temperatures and pressures in a

variety of aqueous fluid compositions has direct application to radioactive waste disposal; hydrothermal uranium deposit genesis, uranium resource exploration, and solution mining.

The solubility of uranium (IV) dioxide is very poorly defined. It is proposed to experimentally determine the equilibrium solubility of uraninite in aqueous media from 100°C to 500°C and 500 to 1000 bars pressure. A synthetic, stoichiometric uranium (IV) dioxide will be reacted with solution in Dickson hydrothermal equipment. Equilibrium may be tested by sampling of the solution as a function of time and reversibility from undersaturated and supersaturated conditions. Initially, the systems $\text{UO}_2 - \text{H}_2\text{O}$ and $\text{UO}_2 - \text{H}_2\text{O} - \text{CO}_2$ will be investigated and hopefully extended to $\text{UO}_2 - \text{H}_2\text{O} - \text{HF}$ and $\text{UO}_2 - \text{H}_2\text{O} - \text{rock}$ buffer systems. The systems to be investigated have been chosen to approximate important radioactive waste disposal and natural hydrothermal environments.

Experimental apparatus has been built and samples of stoichiometric UO_2 obtained. We are now characterizing the UO_2 . DOE funding is pending.

42. GAS-LIQUID METAL REACTIONS AND INTERACTIONS

Norman A. Parlee, Professor, Applied Earth Sciences

Professional Associates:

R.N. Anderson (San Jose State University)
Prof. D.A. Stevenson (Dept. of Mat. Sci., and Eng.)

Graduate Students:

C.H. Hua* S. Slivinsky
B. Bartholomeusz

*Received PhD during report period.

Agency Support

NSF-DMR 75B0168A01
NSF-MRL through CMR

Technical Objective:

- (1) To measure and predict solubilities and diffusivities of gases (e.g. H_2 , N_2 , O_2) in liquid metals and multicomponent alloys;
- (2) To elucidate the laws controlling the effects of surface active elements (O, S, Se etc.) on the rates of absorption and desorption of gases in stirred liquid metals and alloys and thus to predict these effects;
- (3) To find cheaper ways of making expensive reactive metals (e.g., Ti, U, Zr, Mg);
- (4) To develop better ways of recovery-processing fuel and waste disposal;
- (5) To study selective hydriding, nitriding and oxidizing of reactive metals in liquid metallic solvents.

Approach:

Determination of the thermodynamics and kinetics relations from equilibrated and dynamic systems in the laboratory. Development of methods for quantitative prediction of the behaviour in real industrial systems.

Research Report:

(1) The Prediction of the Effects of Surface Active Elements on Gas-Liquid Metal Kinetics

Graduate Student: C.H. Hua

Rates of gas-liquid metal reactions in metal refining, for example degasification (of N, H) in steelmaking, can be spectacularly affected by surface active elements (S, O, Se etc.). Atoms of these elements form one atom thick "rafts" on stirred metal, and thus limit rates of gas ingress and egress. If the concentration of surface-active elements is high enough then the surface is (practically) completely covered and all gas absorption and effusion (or evolution) ceases. This behaviour has been studied by various researchers by correlating rates with θ the fraction of surface covered, or $1-\theta$ the fraction of free surface. Methods of calculating θ or $1-\theta$ for any bulk concentration of an individual surface-active element, from formulas based on surface tension measurements, were established years ago. The present authors have developed new theory for better understanding of these phenomena and for vastly improved methods of predicting and controlling these effects on rates of gas absorption and desorption.

The first improvement is the development of a method of calculating θ_T and $1-\theta_T$ when two or more surface-active elements are present, e.g. the three element case, S, O, Se. This is important because, for example, both S and O are normally present in steelmaking --and the new method quantifies the "additive" effect.

A theoretical treatment led to the equation $k = MD^{\frac{1}{2}} \sqrt{1-\theta_T}$ where k is the rate constant (for H or N) absorption or desorption, D is the gas atom diffusivity in the metal, and M is a function of the hydrodynamic (i.e. metallo-dynamic) factors liquid density, surface tension and eddy velocity. M is a constant for any particular situation i.e. a certain metal or alloy and stirring rate. Tests show

that known or calculated values of D can be used to estimate rates (k) for different pure iron alloys or gases when the rate for pure iron with one gas is known for a certain M condition.

Plots of rate constants (k) vs. $\sqrt{1-\theta_T}$ are linear, making this form of plotting a superior correlation and prediction method, even though there is obviously a defect in this and all previous theory because plots show that the true equation is $k = D^{\frac{1}{2}} M \sqrt{1-\theta_T} - N$ where N is a small constant, due to the fact that, for all practical purposes, zero rates occur at 96 to 99% of surface coverage rather than 100% as assumed by past theory. Very recent discoveries by Grabke in the field of catalysis explain why rates become zero or immeasurably small at these very high coverages.

Another new method of correlation eliminates the big variability of "metallodynamic" conditions among different researchers. This utilizes a dimensionless "fractional rate constant", e.g. for nitrogen, k_N^F , which has values from 0 to 1. Unity represents metal hypothetically completely free of surface active elements. Plots of k_N^F vs. $\sqrt{1-\theta_T}$ are linear, and values of k_N^F for both nitrogen absorption and desorption in iron and its alloys in the 1600°C range can be represented by $k_N^F = 1.19 \sqrt{1-\theta_T} - 0.19$. One master line-graph, or its equation just above, predicts rates for iron and most of its alloys. The effects of higher or lower temperatures can be calculated. Useful k_H^F vs. $\sqrt{1-\theta_T}$ relations can also be developed for hydrogen in Fe, Cu, and Ni. Very recently Hua and Parlee have shown that the rate of the $\underline{C} + \underline{O} = \text{CO(g)}$ reaction with argon injection is also controlled by this law in the presence of \underline{S} , as are also the very important reactions $\text{O}_2 + \underline{C} = \text{CO}_2$ and $\text{CO}_2 + \underline{C} = 2 \text{CO}$ in steelmaking.

These new equations will make it vastly easier to predict and control rates of industrial degasification by vacuum or by flushing, also the rates of gas injection treatments in liquid metal refining

processes.

(2) Selective Nitriding etc. of Simulated Spent Thorium Reactor Fuel

Graduate Student: Sandra Slivinsky

There are many who believe that thorium will prove to be the most economic and suitable reactor fuel--providing suitable cycles involving reprocessing can be developed. Considerable uranium as well as the various unwanted fission products (F.P.) must be removed before the purified fuel can be returned to the reactor.

R.N. Anderson's Stanford Ph.D. dissertation (1969) demonstrated how spent uranium or uranium oxide fuel could be reprocessed (i.e. purified) and made ready for reuse by a process involving selective nitriding of the U + F.P. in liquid tin solution, separation of the UN, reoxidation of UO_2 and recycling the tin. Plutonium can be returned with the UO_2 to the reactor as fuel.

Present studies deal with selective nitriding aimed at first making a suitable Th-U separation. This will be followed by experiments with simulated fission products in order to develop a desirable three way separation of Th, U and F.P.. Other new methods of separation suggested by Hwang's Stanford Ph.D. dissertation (1980) will also be considered.

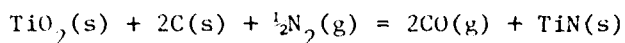
(3) Carbo-Nitrothermic Reduction as a Vehicle for Making Ti and Other Reactive Metals

Graduate Student: B. Bartholomeusz

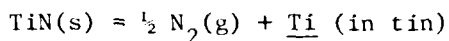
Recently the price of Ti was quoted as \$7.40/lb as sponge and \$9.45/lb as bar, compared with \$0.70 for Al and \$1.00 for Cu. A rough analysis of raw material and process economics gives good reason to believe that cheaper Ti can be made by following steps

discovered by Anderson (Stanford Ph.D. dissertation, 1969) and Parlee--but never further researched because of preoccupation then and since with main thesis project, a new method of reprocessing nuclear reactor fuel.

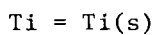
Step 1. Carbo-Nitrothermic Reduction



Step 2. Vacuum decomposition of the TiN in presence of an (Ti) activity depressing solvent



Step 3. Recovery of Ti by fractional solidification, followed by evaporating off most of the tin.



The tin does not need to be all removed because it's an excellent alloying element for Ti. Most of the tin is recycled.

The revived research was started last winter with residual unrestricted research funds. Runs have begun on the study of Step 1. The optimum temperatures, pressures, and gas compositions are being sought. The stoichiometry must also be determined--the nitride formed may be anywhere in the δ range i.e. $\text{Ti}_{0.9}\text{N}$ to $\text{Ti}_{2.6}\text{N}$ -- and is probably controllable within a certain range. Step 2 has been studied thermodynamically in reverse by Hwang (Stanford Ph.D., 1980)--which will be helpful. A full study to establish the probable feasibility and economics will require at least one 3 year Ph.D. research.

A simpler appearing process by Anderson and Parlee involving the first step reaction $\text{TiO}_2(\text{s}) + 2\text{C}(\text{s}) = 2\text{CO}(\text{g}) + \underline{\text{Ti}}$ (in tin etc.) does not appear to be really economic, partly because the concentration of $\underline{\text{Ti}}$ produced is small. The carbo-nitrothermic route would appear to prevent some of these difficulties.

Publications:

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3. N. A. D. Parlee, "Thermodynamics of Reaction, and Interaction Properties in Some Gas-Liquid Metals Systems," Proc. of Workshop on Techniques for Measurement of Thermodynamic Properties, U.S. Bureau of Mines, Albany, Oregon, August 1979 (in press).
4. C. H. Hua and N. A. D. Parlee, "Prediction of the Effects of Surface-Active Elements in Gas-Liquid Metal Reaction Kinetics," Met. Trans. (1981) (in press).

43. ELECTRICAL, OPTICAL AND METALLURGICAL PROPERTIES OF SEMICONDUCTING MATERIAL

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Graduate Students:

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*Received Ph.D. during report period

Agency Support:

Navy N00014-78-C-0297

AROD DAAG-78-C-0018

NSF DMR-79-01661

SERI XI-9-8030-1

Technical Objective:

To prepare new semiconducting materials, measure their pertinent properties, and construct novel devices therefrom.

Research Report:

(1) Rectification in $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ N-n Heterojunction Devices.

Graduate Student: S. C. Lee

The previously unsolved problem of rectification at $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ N-n heterojunctions is found to originate from a vague concept regarding the maximum junction grading width which can sustain rectification. The theoretical current density versus voltage characteristics of this heterojunction system are derived from thermionic emission theory. It is found that, unless the impurity concentration of the AlGaAs layer (prepared by LPE techniques) is less than 10^{16}cm^{-3} , typical 90 to 200 metallurgical grading widths at the N-n heterojunction interface produce either ohmic or poorly rectifying characteristics. These results explain (1) the lack of rectification in most N-n $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ heterojunctions reported in the literature and (2) the recent observation of

significant rectification in high purity (N)Al_{0.3}Ga_{0.7}As-(n)GaAs heterojunctions reported by Chandra and Eastman.

(2) Current-Voltage Characteristics of Al_xGa_{1-x}As Schottky Barriers and p-n Junctions.

Graduate Student: S. C. Lee

Studies of temperature-dependent current-voltage characteristics of Al_xGa_{1-x}As Schottky barriers and p-n junctions indicate a gradual departure from theoretical behavior with decrease in temperature. The diode ideality factor n , which takes values between 1 and 2 at room temperature, increases to values between 1.5 and 4 at 94 K. It is shown that, if the ideality factor-ambient temperature product is replaced by an appropriate effective temperature T^* , the I-V data appear to obey the theoretical formulae at all temperatures. The fact that T^* is larger than the ambient temperature may be due to joule heating at the rectifying junction. It is also shown that the $1 kT$ I-V characteristic of a p-n diode can be described either by standard diffusion or thermionic emission theory. This enables one to determine the barrier heights of p-n diodes from their $1 kT$ I-V plots.

(3) Electron Transport Properties of Al_xGa_{1-x}As.

Graduate Student: K. G. Jew

The goal of this project is to perform a systematic study of the transport of free carriers in Al_xGa_{1-x}As. Previous work on the electrical properties of Al_xGa_{1-x}As have usually been over a limited range of alloy compositions, concentrating on the properties of n-type material in the direct bandgap range where $x < 0.4$. Past work has usually taken into consideration only the Γ and X conduction band minima, but recent studies have shown that the L minima also contribute over a certain composition range. A detail model for electronic transport in Al_xGa_{1-x}As should include all three Γ , L and X bands. Presently, work is continuing on the analysis of the electrical properties of both n-type and p-type Al_xGa_{1-x}As as both composition and temperature are varied.

The approach being followed makes use of the relaxation time approximation. The scattering mechanisms are described by relaxation times and are combined to give a calculated mobility which can then be compared with experimentally measured mobilities. The temperature dependence of the mobility is analyzed to determine the relative contributions of each of the scattering mechanisms to the total mobility. Since many of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ parameters needed for the transport calculations are uncertain, we have worked at obtaining more reliable values by fitting the calculated results to the experimental data.

The electrical properties of p-type $\text{Al}_x\text{Ga}_{1-x}\text{As:Ge}$ have been characterized by Hall measurements to obtain the carrier concentration and mobility as temperature is varied. The temperature dependence of the carrier concentration has been analyzed to obtain the dopant compensation ratio and the ionization energy. The temperature dependence of mobility is analyzed to determine the strengths of the scattering mechanisms. For the valence band, the major contributions are from polar-optical, nonpolar-optical, deformation potential, ionized impurity and alloy scattering. Work is continuing on determining the composition dependence of the transport parameters.

In n-type $\text{Al}_x\text{Ga}_{1-x}\text{As}$ where the Γ , L and X minima can all be involved in carrier transport, the analysis is complex. In the range $x < 0.3$, carriers in the Γ minima are dominant. In the range $x > 0.7$, carriers in the X minima are dominant. In the intermediate range $0.3 < x < 0.7$, carriers in all three Γ , L and X minima need to be considered. The contribution of carriers in each valley to the total mobility needs to be separated out. We have been working at characterizing the major scattering mechanisms which affect the mobility in each valley. In the Γ minima, the major scattering mechanisms are polar-optical, deformation potential, ionized impurity and alloy scattering. In the X minima, we need to include intervalley, polar-optical deformation potential, ionized impurity and alloy scattering. Properties of the L minima are not well known but the main scattering mechanisms are expected to be the same as those in the X minima. Current effort is directed toward understanding the composition dependence of the transport parameters by comparing calculated and experimental results.

(4) Preparation and Properties of Semi-Insulating AlGaAs:Cr/GaAs Heterojunctions and MIS Devices

Graduate Student: M. I. Landstrass

The objective of this research program is to prepare semi-insulating $\text{Al}_x\text{Ga}_{1-x}\text{As:Cr/GaAs}$ heterojunctions and to determine their utility for MISFET applications. The major emphasis has been placed on characterizing the mobile and immobile space charge layers at the heterojunction interface, thus enabling one to determine the band structure and transport properties unique to the heterojunction.

Semi-insulating (SI) $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As:Cr}$ layers were grown by liquid phase epitaxy. 0.5 mole percent Cr was added to a closely compensated AlGaAs melt. Close compensation of the n- and p-type impurities was achieved by baking out the AlGaAs melt in flowing H_2 for approximately 100 hours prior to the addition of Al and As.

The $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As:Cr}$ layers grown in this study were 0.8 μm in thickness. Due to the thinness of the layer, electrons (or holes) are also trapped at the free surface as immobile charges and at the GaAs side of the interface as mobile charges. This added source of compensation makes for very reproducible growth of crystals with a resistivity of approximately 1×10^{11} ohm-cm. Most heterostructures were ohmic at low fields and dominated by Fowler-Nordheim tunneling at higher fields.

C-V measurements from 10Hz to 1MHz were performed on Au-Cr/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As:Cr/GaAs}$ MIS capacitors for both n- and p-type GaAs layers. No measurable dispersion or distortion of the characteristics due to interface states was detected. Both n- and p-type GaAs capacitors were always found to be accumulated at zero bias. This is attributed to the fixed charge present in the AlGaAs:Cr layer due to the small fraction of residual donors (or acceptors in p-type GaAs) that have not been compensated by the Cr traps. G-V measurements were also performed from 10 Hz to 1 MHz on the MIS capacitor samples. Since the dominant transport across the interface in these samples is due to Fowler-Nordheim tunnelling, the conductance is a direct measure of the density of occupied states at the interface.

The conductance results on the n-type GaAs capacitors indicated two main peaks. The one occurring at negative bias corresponded to the gate voltage calculated for the onset of the formation of a hole inversion layer. The other, occurring at positive bias, was split into a doublet and appeared in the voltage range corresponding to strong accumulation of electrons. This doublet was located at an energy 0.10 eV above the conduction band edge with an energy splitting of approximately 0.0086 eV. This peak is taken as direct evidence of quantization of the conduction band into sub-band levels with population of the ground and first excited sub-band state occurring at room temperature.

In order to corroborate the results of the MIS capacitor measurements, inversion mode transistors were fabricated from $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}/(\text{n})\text{GaAs}$ layers. This structure was chosen because of the low processing temperatures required to form Zn diffused p^+ source and drain contacts to the hole inversion layer. Such transistors were characterized by measuring the drain-source current as a function of the gate voltage and by measuring the gate-drain capacitance. All measurements were consistent with a p-channel inversion mode FET having a threshold voltage of -3.0 volts and demonstrate the viability of the heterojunction approach to inversion mode transistor operation using GaAs. The first order theory of inversion mode transistor operation was found to apply. The only major deviation was a large increase in hole mobility at large gate voltages.

The major reason that GaAs MISFET technology is of interest is due to the large electron mobility (4000 to 8000 $\text{cm}^2/\text{V}\cdot\text{sec}$ at 300 K) coupled with its large bandgap (1.4 eV). For this reason a mobility study of both inversion and accumulation layers at the $\text{AlGaAs}/\text{GaAs}$ interface was initiated.

The most complete part of this study to date has been the characterization of electron accumulation layers at the heterojunction interface. This was of interest because previous tunneling spectroscopy of this system showed that the electrons reside in sub-band states due to quantization of the conduction band at the interface. The other motivation for this study was that there are extensive reports in the

literature related to this system, thus enabling a common reference point with other work.

The study consisted of measuring the Hall mobility and carrier concentration of the combined heterostructure as a function of temperature from 5 to 300 K and then stripping off the AlGaAs layer, measuring the GaAs layer and finally subtracting to get only the contribution from the interface electrons. A structure was chosen that had been shown from C-V measurements to have an electron accumulated surface at zero bias.

The major result of the study was that the interface electrons were shown to have a very high mobility ($30,000 \text{ cm}^2/\text{V-sec}$) for sheet electron densities of $5 \times 10^{12} \text{ cm}^{-2}$. The mobility varied by only 30% throughout the temperature range while the electron density decreased rapidly on heating from 100 to 300 K. The major finding has been that even though the measurements on the combined heterostructure yield mobility results which infer that the mobility decreases rapidly near room temperature but the electron concentration remains nearly constant, the converse actually occurs as was determined by measuring the contributions from the individual layers. This is due to thermal excitation from a confined to a bulk-like sub-band.

It is found that the decrease in the concentration of high mobility electrons, at higher temperatures, is thermally activated with a characteristic energy of 0.0086 eV which is the energy difference between the two sub-band states.

The effective mass has been measured by other workers and found to be 10% larger for electrons in the sub-band state so that the source of the high mobility must be due to substantially reduced scattering of electrons by both charge impurities and phonons.

The sub-band energy spacing can be increased by application of a substrate bias. Current work involves measuring the mobility and interface electron concentration as a function of sub-band spacing in order to determine how to employ these high mobility electrons in room temperature device operation.

(5) Fundamental Studies of Photocarrier Tunneling in GaAs Solar Cell Structures

Graduate Student: Kevin J. Malloy

For the past year, work on this project has been concerned with improving the efficiency of the Cascaded Junction Solar Cell (CJSC). These structures consist of a high band gap p-n junction solar cell in electrical and optical series with a low band gap cell. The optical and electrical series interconnection is provided by a high band gap tunnel diode. Currently, the AlGaAs top cell and GaAs bottom cell structure shows the most promise. However, performance of this CJSC under multi-sun concentration is limited by ohmic losses in the AlGaAs tunnel junction. Our work has been aimed at improving this tunnel junction by understanding the materials and electronic properties of heavily doped, LPE grown, $n^+ \text{Al}_x\text{Ga}_{1-x}\text{As:Te}$ and $p^+ \text{Al}_x\text{Ga}_{1-x}\text{As:Ge}$. Both photoluminescence and the standard electrical characterization techniques have been used.

The photoluminescence spectra at 77K of Te doped n^+ GaAs shows a peak at 1.24 eV associated with a Ga vacancy--Te impurity complex. At ultra-high doping levels (Te melt concentration greater than 0.1 at % carrier concentration around 10^{19} cm^{-3}), a broad peak at 1.45 eV appears that is due to impurity band formation and band gap narrowing in the material. Observed here, for the first time in photoluminescence, are peaks at 1.62 eV and 1.17 eV, attributed to the microprecipitates GaTe and Ga_2Te_3 , respectively. Further studies with transmission electron microscopy and electron diffraction patterns will be used to verify this result.

As the Al mole fraction, x , is increased, the 1.2 eV peak increases linearly in energy, in agreement with previous studies. The 1.17 eV peak remains independent of x but steadily decreases in intensity, as expected for a transition involving a Ga-Te compound. The 1.62 eV peak becomes obscured by the AlGaAs:Te free hole to bound electron recombination and by the reduction in the Te distribution coefficient with increasing Al composition. A currently unidentified broad peak at 1.45 eV dominates the spectra of AlGaAs:Te for high doping levels. It remains detectable up to $x = 0.6$ when obtaining highly doped AlGaAs becomes difficult.

The primary luminescent transition in p^+ GaAs:Ge at 77K is the free electron to bound hole recombination occurring at 1.468 eV, giving, in good agreement with previous results, a 40 meV activation energy for the Ge acceptor. Band gap narrowing occurs to a lesser extent in GaAs:Ge. The maximum reduction observed was less than 10 meV for 10 at % Ge in the melt and a carrier concentration of 10^{19} cm^{-3} .

Another peak occurs at 1.35 eV in GaAs:Ge. This has previously been reported as due to an As vacancy-Ge acceptor complex. As Ge doping increases, however, the As vacancies are occupied by Ge acceptors and the intensity of this peak is reduced.

The spectra of p^+ AlGaAs:Ge show two near band-edge peaks, about 40-60 meV apart, that are quenched at low temperatures by other radiative and nonradiative transitions. A broad peak independent of x occurs at 1.53 eV. This has been attributed to various Ge acceptor-defect complexes. A peak at 1.43 eV also independent of x also occurs. Other work has attributed this peak to emission from the GaAs:Cr substrate but our current work raises doubts about that identification. As the Ge doping increases, this peak broadens and increases in intensity until it completely dominates the spectra, particularly for $x \geq 0.4$. While it is conceivable that emission from the substrate could be observed, the line width should be independent of the epitaxial layer. Further work will be aimed at characterizing this transition more fully.

Several heterojunction (AlGaAs-GaAs) tunnel diodes were also fabricated. These diodes exhibit a second or third "hump" in their low temperature I-v characteristics. These humps are traditionally attributed to tunneling to impurity states in the band gap. Future studies will be aimed at identifying these impurity states and correlating them with transitions observed in photoluminescence.

Reference Publications

1. S. C. Lee and G. L. Pearson, "Dark-Current Reduction in Heterojunction Diodes," IEEE Trans. on Electron Devices ED-27, 2181 (1980).
2. S. C. Lee and G. L. Pearson, "Dark-Current Reduction in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ Heterojunction Diodes," J. Appl. Phys. 52, 275 (1981).
3. S. C. Lee and G. L. Pearson, "Rectification in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ N-n Heterojunction Devices," Solid State Electronics 24, 563 (1981).

44. ELECTRON BEAM TECHNOLOGY AND MICROSTRUCTURES

R. F. W. Pease, Professor, Electrical Engineering

Graduate Students:

A. A. Iranmanesh
K. J. Polasko
D. B. Tuckerman
Y. W. Yau (Received MS during the report period.)

Agency Support:

ARPA MDA 903-78-C-0128
NSF ECS 79-11100
JSEP DAAG 29-79-C-0047

Technical Objectives:

The general objective of the research performed in this group is to study the physics and technology of finely focused electron beams and their interactions with solid targets and the generation and applications of microstructures. Efforts during the past year have been directed towards exploring the electron optics of axially symmetric lenses with combined magnetic and retarding electric fields, the interactions of low energy electron beams with solids, inorganic electron resists and the use of microstructures as heat exchangers.

Research Report:

(1) Electron Lenses with Combined Magnetic and Retarding Electric Fields

Graduate Student: Y. W. Yau

Probably the most fundamental problem in electron optics is the occurrence of aberrations in electron lenses. Such aberrations not only limit the resolution in electron microscopes but also set a limit to the speed of electron probe systems such as pattern generators and microanalysers. Conventional electron probe systems employ lenses which use purely magnetic focusing. We are investigating lenses in which the target is immersed in a retarding field. Although such a

configuration is not always practical there are a number of applications such as lithography and annealing where it is.

In the past year the following progress has been made:

- Refinement of the computer program used to determine the distributions of electrostatic and magnetostatic potentials.
- Predictions that the coefficients of spherical and chromatic aberration should be reduced roughly in proportion to the ratio of [target potential (with respect to cathode)]/(maximum accelerating potential) thus suggesting that aberrations could be reduced by more than an order of magnitude for low energy ($\leq 5\text{keV}$) beams.
- Experimental verification that such reductions can be realized in practice.

In the coming year our work will be directed towards the following objectives:

- A characterization of the effects of space charge on the generation of finely focused beams of low energy electrons in retarding field systems. This study will be primarily directed at the random trajectory displacements rather than the traditional, refocusable, space charge spreading.
- A characterization of the effects of nonflat targets on the focusing of the retarding field systems.
- An experimental demonstration of the overall capability of retarding field configurations for generating finely focused electron beams.

Reference Publications:

- [1] Generation and Application of Finely Focused Beams of Low Energy Electrons, Y. W. Yau, A. A. Iranmanesh, R. F. W. Pease, K. J. Polasko, submitted to the Journal of Vacuum Science and Technology.

(2) Localized Heating of Solid Targets

Graduate Student: A. A. Iranmanesh

The use of laser beams and electron beams for heating semiconductor materials with temperature cycles which cannot be easily matched by conventional means has been well established. We have been investigating the spatial resolution of the temperature cycle which can be induced in a bulk solid target by a finely focused electron beam. The equivalent case for steady state heating with a laser beam has already been calculated. The electron beam case is complicated by the penetration of the electrons into the solid target.

During the past year the following progress has been made:

- We have carried out experiments to verify computations of the radial and depth distributions of the energy dissipated by the beam.
- We have begun to extend the model for computing the spatial distribution of energy density in a solid target bombarded with an electron beam to include electron energies down to 2keV.
- By combining the results of the experiments on penetration with the analytical approach we have computed (steady state) radial and depth distributions of temperature in silicon (and other) targets bombarded with beams of different energies and current densities. These calculations can easily be extended to include transient distributions in a material with linear thermal conduction.
- We have worked on the problem of numerically computing the transient temperature distributions in targets with nonlinear thermal conductivities bombarded with finely focused ribbon beams. This problem becomes increasingly awkward as the beam width is reduced below 4 micrometers.

In the coming year our work will be directed towards the following:

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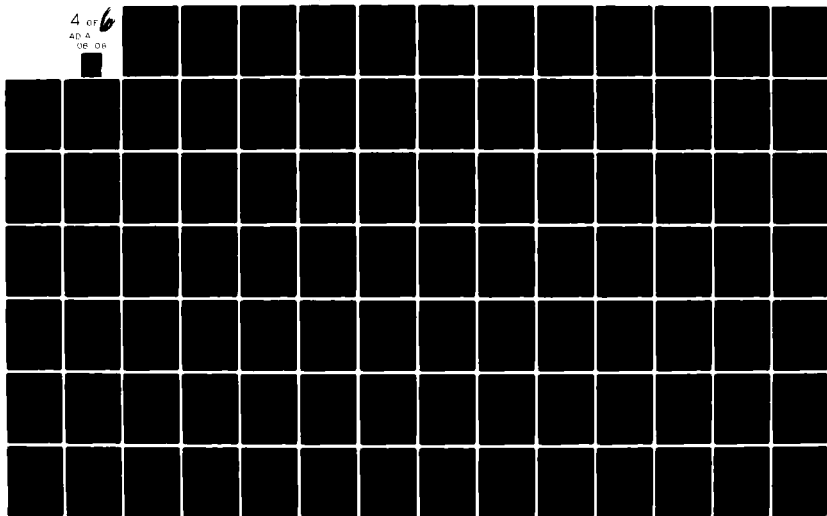
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- Extending the above computational methods to determine the transient spatial distributions of temperature of a target irradiated with a fine beam.
- Designing and carrying out experiments to check the above computations.
- Extending the Monte Carlo simulation of electron scattering in a solid target to beams of lower energies and using the resultant energy dissipation profiles to calculate temperature distribution.

Reference Publications:

- [1] Generation and Application of Finely Focused Beams of Low Energy Electrons, Y. W. Yau, A. A. Iranmanesh, R. F. W. Pease, K. J. Polasko, submitted to Journal of Vacuum Science and Technology.

(3) Inorganic Resists

Graduate Student: K. J. Polasko

The performance of lithographic systems is becoming one of the most crucial aspects of microelectronic fabrication. This performance is largely governed by the sensitivity (usually expressed as the required dose), contrast and resolution of the radiation sensitive material. The polymeric materials which are usually used are already the subject of intense study; therefore we are looking at a class of materials which are radically different and which may yield improved resolution and contrast. The basic mechanism is that radiation induces localized diffusion of silver into a thin film of glass made up of Ge and Se and the diffused regions are selectively insoluble in a subsequent development.

In the past year the following progress has been made:

- We have set up apparatus and have learned the techniques for preparing films of GeSe glasses.
- We have developed techniques (a) for applying thin films of silver without diffusing the silver into the glass (b) for developing films following exposure to

radiation (c) for stripping the silver from the unexposed regions.

- We have investigated, using TEM and sputter Auger analysis the structure and composition of evaporated GeSe films doped with silver.
- We have initiated into the relationships between the required dose and (a) energy of exposing electrons and (b) the concentration of selenium.

In the coming year our work will be directed towards the following objectives:

- Investigate quantitatively the diffusion of silver into Ge/Se compounds using electron microprobe analysis, sputter Auger analysis and other microanalytical techniques. A complementary technique is to study the absorption by the films of tuned synchrotron radiation.
- Study the mechanisms which affect the dissolution of silver into the Ge/Se compounds and hence gain an understanding of the factors which control the sensitivity, contrast and resolution of this class of resist materials.
- Develop appropriate techniques for transferring the very thin diffused silver pattern into a thick relief image using dry processing and eliminating the use of cyanide solutions.

(4) High Performance Heat Exchanging Using Microstructures

Graduate Student: D. B. Tuckerman

One of the fundamental limits on the evolution of integrated circuits to higher densities, speeds and scales of integration has been the upper limit on the power density set by heat dissipation limits. This limit has usually been set at about 20 W/cm^2 for silicon integrated circuits used in a large system. The bulky conventional heat sinks used for individual power devices are not practical for cooling large arrays of circuits. We have investigated the use of silicon

microstructures fashioned directly into the silicon chip to promote much more effective cooling of the circuits.

During the past year the following progress has been made:

- The specific thermal conductivity, in $\text{W/cm}^2 \text{ } ^\circ\text{C}$, was analyzed for a structure consisting of a silicon chip with microchannels etched into the back surface (away from the heat dissipating circuit) and with water flowing laminarily through the channels. The results indicated that a dramatic improvement should be possible and that for a channel length of 1 cm. the optimum channel width should be about 0.05 mm and that the height of the channels should be about 0.35 mm, i.e., about the thickness of a standard silicon chip.
- For an input pressure of about 30 p.s.i. a specific thermal conductivity of 11 $\text{W/cm}^2 \text{ } ^\circ\text{C}$ should be achievable.
- A set of experiments was designed and carried out which confirmed the theory and whose results lead us to believe that this is a very practical way to allow us to increase greatly the power and speed of VLSI. In one experiment 790 W were dissipated continuously in an area 1 cm. x 1 cm. for a maximum temperature rise of only 71 $^\circ\text{C}$.

During the coming year the work will be directed towards the following objectives:

- Investigate the implications of this new degree of freedom to scale VLSI more aggressively, i.e. with increasing power density.
- Investigate the thermal conduction properties of structures with microscopic dimensions especially as those dimensions approach the phonon mean free paths of the materials used.

Reference Publication:

- [1] High Performance Heat Sinking for VLSI, D. B. Tuckerman and R. F. W. Pease, Electron Device Letters, EDL-2, 126 (1981).

45. STUDIES OF THE DYNAMICS OF MOLECULES AND MACROMOLECULES IN LIQUIDS

R. Pecora, Professor, Chemistry

Professional Associates:

S. P. Michielsen*
W. H. Nelson*
C.-C. Wang*

* Left during report period

Graduate Students:

S. E. Bott
A. Flamberg
K. R. Maier
N. H. Oliver

S. G. Stanton
B. E. Zebrowski
K. M. Zero

Agency Support:

NSF CHE 79-01070
NIH 5R01 GM 22517

Technical Objective:

To formulate theories of and to develop experimental techniques for studying the dynamics and motions of molecules in condensed systems.

Approach:

Theories of molecular motions and experimental techniques are formulated in terms of time-correlation functions. Experimental studies are carried out using dynamic light scattering, and other types of fluctuation spectroscopy.

Research Report:

1. Molecular Motions in Glassy Materials

Graduate Student: N. H. Oliver

Experiments and theoretical interpretations of the rotational motion of chlorobenzene in polymethyl methacrylate have been published.^{1,2} The experimental results may be explained by a model in which the chlorobenzene reorientation consists of an initial fast

relaxation (picoseconds) followed by a very slow relaxation. The initial reorientation is basically rotational diffusion in a restricted volume.³ The slow subsequent reorientation represents the coupling of the probe reorientation to the relaxation of the polymer. The reorientation of a longer probe molecule ($\text{Cl}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_5$) in polymethyl methacrylate is now being studied to further test our theoretical interpretation.

2. Hydrodynamics of Rigid Rod Macromolecules

Graduate Student: K. M. Zero

Systematic studies of the concentration dependence of both the rotational and translational diffusion coefficients of three different molecular weights of poly- γ -benzyl-L-glutamate dissolved in ethylene dichloride have been completed.⁴ The results indicate that the rotational diffusion coefficients decrease as the inverse eighth power of the length in the semi-dilute region.

3. Resonance-Enhanced Rayleigh Scattering

Graduate Student: Susan Stanton

Resonance-enhanced Rayleigh scattering has been studied for diphenylpolyenes in CCl_4 , cyanine dyes in ethanol, coumarins in ethanol and nitrophenols in water, ethanol and water-ethanol mixtures. Our results show depolarized scattering cross sections 10-1000 times that of benzene following expected trends with scattering wavelength and oscillator strength of the molecule used.

Nitrophenols are acid-base indicators, so with an appropriate choice of scattering wavelength one form is resonance enhanced while the other is not. This leads to large differences in scattering cross sections. Preliminary results of p-nitrophenol at 488 nm for depolarized scattering are $I_{\text{base}}/I_{\text{acid}} = 10/1$, while for polarized scattering $I_{\text{base}}/I_{\text{acid}} = 3/1$. In addition, a difference in rotational times between the anionic and neutral forms of p-nitrophenol has been observed. This can be studied as a function of solvent to probe the interactions between charged molecules and solvent.

4. Macromolecules in solution

Graduate Students: A. Flamberg
K. R. Maier
B. E. Zebrowski

Experiments have been performed in the past year on

ribonuclease
bovine pancreatic trypsin inhibitor
gramicidin A
polyhydroxy phenylmethanes
polyamic acids
polyacrylic acid
myosin rod.

Work on gramicidin A is complete and the results have been submitted for publication. Solution dimensions of gramicidin in alcohol solutions and changes in these dimensions on adding salt have been determined.

A study of size changes during the thermal denaturation of ribonuclease A has been completed and published.⁵

5. Studies of Surfactant Micelles and Phospholipid Vesicles

Graduate Students: A. Flamberg
S. E. Bott

Dynamic light scattering studies of a variety of surfactant micelles in aqueous salt solutions are in progress. Of major interest is the effect of salt concentration on the size, shape and flexibility of the micelle.

Studies of the fusion of phospholipid vesicles are also currently being conducted.

Reference Publications:

1. A. C. Ouano and R. Pecora, "Rotational Relaxation of Chlorobenzene in Poly(methylmethacrylate) Part I. Temperature and concentration Effects," *Macromolecules* 13, 1167 (1980).
2. A. C. Ouano and R. Pecora, "Rotational Relaxation of Chlorobenzene in Poly(methylmethacrylate) Part II. Theoretical Interpretation," *Macromolecules* 13, 1173 (1980).
3. C.-C. Wang and R. Pecora, "Time-Correlation Functions for Restricted Rotational Diffusion," *J. Chem. Phys.* 72, 5333 (1980).
4. K. M. Zero and R. Pecora, "Rotational and Translational Diffusion in Semi-Dilute Solutions of Rigid Rod Macromolecules," *Polymer Preprints* 22, 98 (1981).
5. C.-C. Wang, K. H. Cook, and R. Pecora, "Dynamic Light Scattering Studies of Ribonuclease," *Biophysical Chemistry* 11, 439 (1980).

46. MATERIAL CHARACTERISTICS OF CANCELLOUS BONE

R. L. Piziali, Associate Professor, Mechanical Engineering

Professional Associates:

L. W. Swenson

Graduate Students:

K. S. Kim

Agency Support:

Veterans Administration

Technical Objective:

To develop a micro-polar type material model for cancellous bone (beam structures). Static and dynamic three-dimensional models are being developed.

47. COMPUTER-AIDED DESIGN OF INTEGRATED CIRCUIT FABRICATION FOR VLSI DEVICES

J. D. Plummer, Associate Professor, Electrical Engineering

Professional Associates:

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J. F. Gibbons	J. D. Meindl
C. R. Helms	K. C. Saraswat
C. P. Ho	W. A. Tiller

Consultants:

B. E. Deal
T. I. Kamins

Graduate Students:

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R. W. Barton	M. M. Mandurah*
G. Bronner	H. Z. Massoud**
S. Chen	F. Mohammadi*
D. Chin	S. Y. Oh*
L. Christel**	J. Rouse**
E. Kutlu	B. Swaminathan

*Received PhD during report period.
**Expect PhD to be completed during report period.

Agency Support:

DARPA - MDA-903-79-C-0257

Approach:

The singular objective of the work described here is the development and implementation in a user-oriented simulation program of process models for small geometry VLSI structures. This work builds upon an established program which has resulted in the release of a second generation process modeling computer program--SUPREM II--which is generally regarded as the preeminent tool of its type available today. It

is used by more than 100 industrial firms and university research groups for the simulation and design of state-of-the-art MOS and bipolar fabrication processes. Work in the present contract year will result in the release of SUPREM III in mid-1981 which, for the first time, will simulate the multi-layer structures used in most modern IC technologies. The development of accurate physical models for SUPREM has been a principal objective of this program for the past five years. The work described here extends these models and their implementation in SUPREM to the small geometry devices and multi-layer structures which are expected to be used in VLSI circuits in the next several years.

The historical trend in silicon integrated circuit technology has been towards increased complexity and smaller active device dimensions. This has resulted today in lateral device dimensions on the order of 2-3 μm and vertical dimensions well below 1 μm in many commercially available circuits. There are no basic physical mechanisms which prevent a reduction in each of these dimensions by an order of magnitude; such device structures are widely projected for the 1985-1990 time period. Such projections are predicated, however, on our ability to understand physically and accurately model the fabrication techniques which will be used in the construction of such devices.

For devices with relatively large geometries ($>5 \mu$) and loose processing tolerances, relatively simple models suffice for prediction of vertical device structures resulting from a given fabrication sequence. As device dimensions shrink, however, it becomes essential to employ more robust process models and to consider the interaction both laterally and vertically of various processing steps, if accurate simulation of structures is to be obtained. This is important even with today's 2-3 μm device geometries; it will become essential for smaller devices.

Large geometry devices can be successfully modeled as one-dimensional structures. This is true for both process models and electrical models. Devices with lateral dimensions below a few microns, however, require two-dimensional models for accurate simulation. This need has stimulated a large body of work in recent years on

two-dimensional electrical models of device current-voltage characteristics. This work has resulted in remarkable advances in our understanding of small geometry device physics.

Progress has not been as rapid, however, in two-dimensional process modeling. This is a direct result of our need for improved physical models of oxidation, ion implantation, diffusion, and CVD. It is quite clear that these processes are not one dimensional. Recent experimental evidence has clearly indicated that oxidation or impurity diffusion in a localized region of a silicon substrate can substantially affect oxidation or diffusion rates in laterally or vertically adjacent regions of the substrate. There is no clear agreement at the present time on the basic physical mechanisms responsible for such results. It is clear, however, that we must quantitatively understand such phenomena if we are to accurately model small device structures.

A specific goal of this program is to understand and model these two-dimensional effects. We have made substantial progress in this regard in the past year. It appears now that the basic physical phenomena underlying these interactions are the roles of point defects--silicon vacancies and interstitials--in impurity diffusion, thermal oxidation, and other processes. The generation and consumption of these point defects during high temperature fabrication steps appear to be the unifying physical effects which can explain many of the phenomena which have been regarded as anomalous to date. We have used such models to quantitatively understand a variety of process phenomena and have incorporated some of these models in SUPREM II. More such models will be in SUPREM III. The unifying role of these mechanisms is a cornerstone of the work in this program. We regard such models as absolutely essential to accurate modeling of two-dimensional effects in small devices.

In this context, the overall objectives of this program are:

- (1) To develop accurate physical models for the basic technologies used in the fabrication of silicon integrated circuits--oxidation, ion implantation, diffusion, and chemical vapor deposition (CVD).

- (2) To develop accurate physical models for the interaction of these processes, for example, the enhancement of diffusion coefficients in an oxidizing ambient.
- (3) To develop accurate physical models based upon silicon point defects for two-dimensional process phenomena in small geometry devices.
- (4) To develop high resolution analytic tools for the experimental characterization of small device structures.
- (5) To implement improved process models in SUPREM III so that this program is capable of accurately simulating small devices and multi-layer structures.

Most of the accomplishments in the past year are described in detail in reports which are available to the interested reader [1, 2, 3]. They are listed here specifically in concise form. Activities during the present year have been grouped under five major areas--Thermal Oxidation, Ion Implantation and Diffusion, Chemical Deposition, Materials Research and Interface Physics and SUPREM Implementation. The specific accomplishments are grouped this way as well.

A. Thermal Oxidation

- (1) The oxidation kinetics of silicon at high pressure in a pyrogenic steam ambient have been characterized. Temperature range 800-1000°C. Pressure range 1-20 atm.
- (2) The linear-parabolic oxidation model was applied to oxidation at high pressure and has been found suitable for incorporation into SUPREM.
- (3) Oxide charge densities were characterized for oxides grown in high pressure pyrogenic steam. Post-oxidation charge annealing in inert gases at 800-1000°C was carried out.
- (4) A new experimental furnace with an in-situ Ar/HCl etching capability for the study of thin oxide kinetics and charges was installed and characterized. Reproducible growth kinetics and

charge densities were obtained independent of pre-oxidation cleaning procedure.

- (5) Metal semiconductor work function differences for (111) and (100) oriented wafers were measured and found to be different for the two orientations and possibly dependent upon fixed oxide charge density Q_f .
- (6) Thin oxide growth kinetics for $700^\circ\text{C} \leq T \leq 1000^\circ\text{C}$ and $0.01 \leq P \leq 1$ atm have been experimentally determined. (This work is ongoing at the present time in collaboration with E. A. Irene of IBM and should be largely completed within the present contract year.)
- (7) A theoretical analysis of the initial transient distribution for $dx/dt = \text{constant}$ of both interstitials (fast diffusers) and impurities (slow diffusers) has been completed to help describe the thermal oxidation process.
- (8) A theoretical analysis of the OED effect has been completed and an analytic expression describing this phenomenon derived.
- (9) Experimental data on oxidation enhancement via a gas discharge and via UV radiation has been obtained. (This work is presently under way and will continue into next year.)

B. Ion Implantation and Diffusion

- (1) The Boltzmann transport equation modeling (TE) of ion implanted range statistics has been extended to include an improved hybrid nuclear cross section, wide angle nuclear scattering and electronic scattering.
- (2) TE modeling of range statistics has been applied specifically to the problems of knock-on ions (recoils) and channeling tails. In the first case, excellent agreement with published experimental results has been found. In the second case, agreement with experiment is promising but further work is required.
- (3) A simplified version of the TE approach has been adapted for incorporation in SUPREM III. (This work is currently under way and should be largely completed within the present contract year.)

- (4) A temperature tolerant metallurgy using WSi_2 has been developed for experimental characterization of transient process phenomena. Both MOS and pn diode structures have been found to be stable even after repeated temperature cycling up to 1000°C . This technique is presently being applied to specific problems of interest, including damage annealing and the effects of residual damage on device electrical characteristics.

C. Chemical Vapor Deposition

- (1) A new model has been developed to predict the segregation of arsenic, phosphorus, and boron at the grain boundaries of polycrystalline silicon, as a function of processing parameters such as temperature, grain size, doping density, etc. All of the parameters entering into the model have been determined.
- (2) A new model for carrier transport in polycrystalline silicon has been developed. This model proposes an additional barrier apart from the potential barrier caused by carrier trapping at the grain boundaries through which the carriers have to tunnel. This barrier is caused by the presence of grain boundaries, which disrupt an otherwise continuous lattice structure.
- (3) By combining dopant segregation, carrier trapping, carrier tunneling through the grain boundaries and passivation of grain boundaries by the segregated dopant atoms a complete model has been developed to explain the electrical conduction in polycrystalline silicon. The theoretical model has been compared to experiment and shown to accurately predict the resistivity of polycrystalline-silicon films as a function of dopant concentration, type of dopant and processing temperatures.
- (4) Preliminary data has been obtained in the studies of dry and wet thermal oxidation of polycrystalline-silicon in the temperature range of 750 – 1100°C .
- (5) A study of the thermal oxidation of MoSi_2 and TaSi_2 is being done to determine the mechanism of oxidation.

- (6) Work on contact resistance between WSi_2 and boron and phosphorus doped Si has been started.
- (7) WSi_2 gate enhancement and depletion mode MOS transistors have been fabricated successfully and characterized.

D. Materials Research and Interface Physics

- (1) Measurements of the chlorine distribution in selected SiO_2 samples thermally grown in O_2/HCl mixtures were completed. A physical model for chlorine incorporation into growing SiO_2 layers was developed.
- (2) In conjunction with (1) above, measurements and modeling of electron beam effects on the chlorine distribution in SiO_2 were completed. It was determined that Auger electron spectroscopy studies of Cl and SiO_2 can be performed successfully if electron beam conditions are properly chosen.
- (3) Electron spectroscopy studies of the physical properties of the silicides of tungsten and SiO_2 layers grown on WSi_2 surfaces were completed.
- (4) Experimental and theoretical studies of the redistribution of phosphorus during the thermal oxidation of silicon were completed.

E. SUPREM Implementation

- (1) The first demonstration of a multilayer simulation capability to be included in SUPREM III was demonstrated and tested for poly oxidation and simultaneous phosphorus diffusion out of the poly into the bulk.
- (2) Experiments using polycrystalline diffusion sources were performed to characterize the OED effects in the presence of grain structure at the oxide interface. Results showed that point defect concentrations in the bulk are reduced as indicated by smaller fractional OED in the bulk.
- (3) SUPREM has been rewritten to accommodate multilayer models as well as more extensive capabilities for models and multiple species kinetics.

- (4) Both the SEDAN (one-dimensional) and GEMINI (two-dimensional) device analysis programs have been released and distributed widely. Both programs are directly compatible with SUPREM.
- (5) The capabilities in SUPREM for optimization have been documented and tested for a variety of conditions including physical model parameter extraction as well as technology design applications.

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48. MICROMECHANICAL MODELS FOR THE EXPANSIVE PROCESS IN EXPANSIVE CEMENT CONCRETE

C. W. Richards, Professor, Civil Engineering

Graduate Students:

M. D. Cohen*

*Received PhD during report period.

Agency Support:

NSF ENG 77-03947

Technical Objective:

To explain the expansive process in calcium sulfoaluminate expansive cements and to develop a model incorporating the kinetics of expansion which will allow more realistic predictions of expansion, both normal and abnormal.

Approach:

Continuation of study of the effects of parameter variations on free expansion behavior of cement pastes. A series of blends has been designed to produce specific types of behavior, based on the results of previous analysis. Blends include a) expansive clinker, ground to specific controlled particle size distributions, b) sulfate sources of known characteristics (e.g., reagent grade calcium sulfate hydrates), and c) ordinary Portland cement or Portland clinker. Specimens are made by mixing a given blend with water to give the desired water/cement ratio and casting in molds. During the hardening/expanding process the following properties of the pastes are monitored:

- a. Free expansion
- b. Dynamic modulus of elasticity
- c. Formation of ettringite (by XRD and by chemical extraction)
- d. Nonevaporable water content
- e. Morphology of ettringite crystals (by SEM)
- f. Presence of microcracks (by SEM)

Research Report:

1. In normal expansion the expansion is associated directly with the formation of ettringite and expansion stops when ettringite formation stops.

2. Abnormal expansion occurs when the expansion exceeds that permitted by the strength of the CHS gel, which results in micro-cracking of the gel.

3. The amount of drying shrinkage in hardened expansive cement paste is independent of the amount of expansion, suggesting that expansion is not caused by swelling of colloidal ettringite, as is reported by P. K. Mehta.

4. The time of expansion varies linearly with a) the reciprocal of the Blaine Specific Surface of the expansive component, and b) the initial concentration of calcium sulfate in the cement.

5. Expansion is markedly dependent on the particle size distribution of the expansive component, indicating that it is not caused by swelling of colloidal ettringite (cf. item 3 above). There is an optimum particle size for the expansive clinker which results in maximum expansion.

49. PROTEIN ADSORPTION TO POLYMER FILMS

C.R. Robertson, Professor, Chemical Engineering

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J.C. Wright

Undergraduate Students:

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*Received M.S. degree during
report period

Agency Support:

NIH

Technical Objective:

To develop a new technique for the quantitative investigation of protein adsorption to polymer films.

Research Report:

Protein Adsorption to Polymer Films

Graduate Students: B.K. Lok, Y.L. Cheng

Undergraduate Students: J. Knapp

The initial event upon contact of blood with an artificial surface is the immediate deposition of a layer of plasma proteins. Often the compatibility of such a surface may be correlated to the type and amount of protein originally deposited. For this reason, protein adsorption to several important materials is being studied using a total internal reflection fluorescence technique. Based on the same physical principles as Multiple Attenuated Infrared Spectroscopy, the

adsorption of a fluorescently labeled specie (in this case a protein -- fluorescein isothiocyanate complex) may be followed continuously.

Experiments using this technique are devoted to developing adsorption isotherms for protein adsorption under both static and laminar flow conditions. Later studies will be expanded to cover a broader range of biomaterials and adsorption conditions.

Reference Publication:

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50. SPECTROSCOPY AND QUANTUM ELECTRONICS

A. L. Schawlow, J.G.Jackson-C.J.Wood Professor of Physics
T. W. Hansch, Professor of Physics

Professional Associates:

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H. Gerhardt (Germany), Visiting Scholar
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Graduate Students:

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D. J. Jackson *	J.C-C. Tsai*
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* Received Ph.D. during
Report period

Agency Support:

NSF PHY-80-10689
NSF PHY-78-25552
U.S. NAVY - ONR N00014-78-C-0405

Technical Objective:

To study the interaction between electromagnetic radiation and matter, to extend the range of coherent light techniques, to apply coherent and conventional light to elucidate problems in atomic, molecular and solid state physics.

(1) High Resolution Spectroscopy of Atomic Hydrogen

Visiting Scholar: Dr. B. Couillaud
Dr. A. Siegel

Current research is directed toward measuring the wavelength of the hydrogen 1S-2S transition with higher accuracy, by using a continuous, rather than pulsed, laser. This requires a continuous-wave laser source at a wavelength 2430 Angstroms, but there is no known laser operating at that wavelength. Moreover, there is no crystal that gives good phase-matching for harmonic generation of that wavelength. Ammonia dihydrogen phosphate (ADP) cooled close to its Curie temperature can provide sum-frequency generation of blue light from a krypton laser and yellow light from a dye laser. There have, however, been persistent problems with rapid damage of the surface of the mixing crystal. Some relief was obtained by cleaving the crystal in vacuum and coating the surfaces with evaporated magnesium fluoride. But this treatment is insufficient to permit pumping by the recently acquired ring dye laser, or indeed by any dye laser that gives enough power to carry out the experiment. It was hoped that adequate power levels will be obtainable by using even greater precautions to ensure that the crystal surfaces are clean and completely free from oil films, but this has not been successful, so far. We are now investigating optical mixing processes in room-temperature crystals, to see if the desired ultraviolet wavelength can be obtained with less surface damage.

(2) POLINEX (Polarization Intermodulation) Spectroscopy

Graduate Student: D. R. Lyons
Visiting Scholars: A. Siegel
Z.-Y. Wang
G.-Y. Yan

A new method of Doppler-free spectroscopy has been developed, which is particularly useful when studying atoms in metastable states. As in other methods of nonlinear laser spectroscopy, such as the intermodulated fluorescence technique, it uses two counterpropagating

beams from the same tunable laser. However the relative polarization is modulated, rather than the amplitudes of the beams. The method eliminates most of the Doppler-broadened background, which often obscures Doppler-free spectra from long-lived atomic states. It has been applied to several substances, including neon and copper (using a hollow-cathode discharge for the latter).

(5) Measurement of Wavelength of Pulsed Lasers

Graduate Students: K. M. Jones
L.-S. Lee

It is desired to be able to measure the wavelength of each individual pulse of a dye laser. These pulses typically have lengths of only a few nanoseconds, and so moving-mirror techniques are not applicable. Instead, we are investigating a new technique using three wedge interferometers, one above the other. A collimated light beam illuminates the three interferometers and produces three interference patterns, one above the other, on the cathode of a television pickup tube (vidicon). The image is captured and digitized in the time of a single television frame, and stored in the memory of a microcomputer. Fringes from a wavelength-standard laser are recorded at the same time. Preliminary tests have shown an accuracy of about one part in 500,000, and the ability to track a laser as it is tuned.

(4) Color Center Lasers

Graduate Students: D. J. Jackson
Y. B. Zambre
Visiting Scholar: Dr. H. Gerhardt

A continuous-wave laser, using stimulated emission from color centers in alkali halide crystals, has been used for spectroscopy in the near infrared. A number of helium and hydrogen lines have been

used for spectroscopy in the near infrared. A number of helium and hydrogen lines have been observed by optogalvanic detection. The sensitivity to small numbers of atoms is good, although even the lower levels of these transitions are not very far from ionization. However, in a discharge the helium lines are broadened by the Stark effect of the electric field in the discharge.

A repetitively pulsed electron beam has been constructed. When the photomultiplier is gated to be sensitive at a time between the 5 ns electron beam pulses, much narrower lines are observed.

(5) Doppler-Free Spectroscopy in Hollow-Cathode Gas

Postdoctoral Research Affiliate: J. E. Lawler
Visiting Scholars: Dr. B. Couillaud
Dr. A. Siegel

High resolution spectra, free from Doppler broadening, have been obtained inside the hollow cylindrical cathode of a low-pressure discharge tube. The cathode has a large diameter (3 cm), in order to permit operation at low gas densities, so as to minimize pressure broadening. As in other Doppler-free techniques, the laser beam is divided into two parts, which are sent in opposite directions along the same line through the discharge. Simultaneous absorption of light from both beams by one atom can occur only for those atoms which have zero velocity component along the beam direction. The lines have been observed optogalvanically, by the change in the discharge current. They have also been observed with good sensitivity by intermodulated fluorescence from the level to which they are raised by absorption of the laser light.

The hollow-cathode is especially suited for observation of the spectra of refractory metals. We have observed and measured hyperfine structures and isotope shifts in atomic molybdenum, zinc and copper by this method. The POLINEX method of Doppler-free spectroscopy has been

used with the hollow-cathode discharge.

(6) Doppler-Free Spectroscopy in Radiofrequency Discharges

Graduate Student: D. R. Lyons

Visiting Scholars: Z.-Y. Wang

G.-Y. Yan

We have detected Doppler-free spectra of absorption lines from high states excited in a radiofrequency electrodeless discharge. Such a discharge is especially suitable for use in studying corrosive gases which may attach metallic electrodes or seals. Absorption of laser light is seen by a change in the discharge impedance, which changes the amplitude of the r.f. oscillator. The sensitivity is comparable with other methods of Doppler-free spectroscopy.

(7) Sensitive Intracavity Absorption Spectroscopy

Graduate Student: W. T. Hill

It has been shown previously that a broadband dye laser, without tuning elements, is a particularly sensitive detector for weak absorption lines of any substance inside the resonator. In such a laser, there are very many modes of oscillation competing for the supply of excited molecules. Any slight additional absorption causes the oscillation to cease at the absorbing wavelength. Indeed, the absorption lines from water and oxygen in the air of the laboratory are observed so strongly as to obscure anything else in their region, even in the visible where we usually consider air to be completely transparent. We have, therefore, constructed an untuned dye laser in a hermetically sealed box. The laser can be filled with any gas of

interest, and can be operated at pressures as low as 50 torr. With it, we have resolved fine structures of closely-spaced lines in oxygen, and have measured isotope shifts of weak lines in oxygen 16 and oxygen 18. This project has been essentially completed.

(8) Excited Electronic States in Molecular Sodium

Graduate Students: N. W. Carlson
A. J. Taylor
K. M. Jones

A pulsed dye laser has been employed to excite a chosen level in the A electronic state of the diatomic sodium molecule. As the laser is polarized, the excited molecules are oriented so that they can alter the polarization of a probe beam at any wavelength corresponding to transitions to a still higher electronic level. Probe delays of several nanoseconds distinguish lower-level depolarization from upper-level depolarization.

A large number of new excited states in Na_2 have been identified by this technique, and their constants have been measured.^{1,2} Two sequences of Rydberg states have been observed, each of which permits a good extrapolation to the constants of the molecular ion.

¹N.W.Carlson, A.J.Taylor, K.M.Jones, and A.L.Schawlow, to be published.

²A.J.Taylor, K.M.Jones, and A.L.Schawlow, submitted to Optics Communications (1981).

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3. A Hollow Cathode for Doppler-Free Spectroscopy (J.E.Lawler, A.Siegel, B.Couillaud, and T.W.Hansch), *J. Appl. Phys.* (accepted 1981).
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51. INTERACTIONS OF OPTICAL AND ACOUSTIC RADIATION WITH SOLIDS

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ARCO

Research Report:

(1) Optical Fiber Devices

The guiding of light, the interaction of light waves and vibrational waves, and laser amplification of light waves, in glass fibers and single crystal fibers, are being studied and applied to prototype devices for sensing, signal processing and communication. The spacial coherence and optical scattering properties of single mode optical fibers are being studied in connection with the use of these fibers in interferometry for sensor systems, resulting in some important advantages in system performance. An important example is a Sagnac interferometer which we have demonstrated, in which all components, which include a sensing loop, directional couplers, power splitters, polarizers, polarization controllers, and phase modulators are constructed on a single unbroken 600 meter length of optical fiber. This provides

minimum optical scattering and high signal-to-noise ratio, resulting in sensitivity to rotation which sets the current state of the art. This represents perhaps the first all solid-state, all single mode optical system. Dispersion in fibers, and the control of dispersion, are under study, aimed at achieving large memory times and very high speed operation in optical signal processing, and prototype signal processing systems are being tested. In all these cases, the very low propagation loss in optical fibers is an important factor in achieving high performance devices.

Research is being carried out in the growth of single crystal fibers of neodymium doped yttrium aluminum garnet, in cooperation with Professor R. Feigelson in the crystal laboratory of the Center for Materials Research, using laser-heated pedestal growth apparatus constructed especially for this purpose. We have grown fibers of good internal quality in lengths of several inches and diameters ranging from 250 microns to less than 50 microns. We have measured internal optical amplification in these fibers which agrees with theoretical predictions, and is expected to form the basis for new optical amplifiers and oscillators for use in fiber optic systems of the above kinds. We have shown that optical propagation loss in these fibers depends on surface scattering, which has led to a new phase of work which is now in progress. This involves reducing the diameters of single crystal fibers substantially below the current range of approximately 50 microns, reducing diameter fluctuations as a function of fiber length, developing means for cladding these fibers with suitably controlled index material, and investigating possible diffusion techniques for profiling the optical index as a function of radius within the fiber cross section. These activities are aimed at reducing the number of optical propagating modes which the fiber can support, and decreasing the optical linear scattering loss within the fibers.

(2) Acoustic Waves Devices

The electrical and acoustic wave properties of the polymer polyvinylidene fluoride, PVF_2 , are being studied and used in the design of experimental acoustic transducers and acoustic imaging arrays for the

nondestructive testing of materials. PVF_2 is a semicrystalline polymer which is of considerable interest in a number of fields because of its unusual dielectric, piezoelectric, pyroelectric and nonlinear optical properties. Acoustic imaging as being pursued here represents a new field of application. Its attractiveness for this purpose is its relatively strong piezoelectricity, comparable to that of crystalline quartz, its low acoustic impedance and velocity, its mechanical flexibility and the fact that it can be fabricated in thin films of large size. Its high piezoelectric activity results from the fact that it can crystallize in forms having high dipole moment.

PVF_2 films are produced under the polymer thrust program in the Center for Materials Research, and their properties and transducer applications are being studied under the current program. We have demonstrated ultrasonic transducers using PVF_2 films as the active element, operating in the megahertz to tens of megahertz frequency range, having unique bandwidth, impulse response, and beam shape accuracy. These results have been extended to the design of a prototype multielement imaging array, containing 40 active elements, operated as a phased array for beam forming and scanning. A multilevel digital electronic system under computer control delivers signals with desired phase and amplitude profiles to the individual elements of the array, producing a 2.3 MHz ultrasonic beam in a water tank which is focused to a spot and scanned electronically over the object under study. A novel feature of the imaging array is the use of photolithography to define the elements, to exploit the high accuracy of the photoreduction process, and the ease of construction and simple mass replication capabilities of photolithographic techniques used in standard microcircuit fabrication and in surface acoustic wave device fabrication. This appears to be the first fully operational ultrasonic imaging array using these integrated circuit techniques, and taking advantage of the unique combination of extreme accuracy and extreme simplicity made possible through the use of PVF_2 film. The sensitivity of PVF_2 arrays, although lower than that of ceramic PZT arrays is adequate for a large number of purposes in nondestructive testing and related fields. It is expected that arrays of this type will find very substantial application in practical systems,

where their high accuracy and low cost will be of importance. Immediate extension to arrays having an arbitrary number of elements would be straightforward.

Reference Publications:

1. C. C. Cutler, S. A. Newton, and H. J. Shaw, "Limitation of Rotation Sensing by Scattering," Optics Letters 5, 11, 488-490 (November 1980).
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3. H. J. Shaw, D. Weinstein, L. T. Zitelli, C. W. Frank, R. C. DeMattei, and K. Fesler, "PVF₂ Transducers," 1980 IEEE Ultrasonics Symposium Proceedings, p. 927.
4. R. A. Bergh, H. C. Lefevre, and H. J. Shaw, "All Single Mode Fiber Optic Gyroscope," Optics Letters 6, 4, 198-200 (April 1981).
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52. MECHANICAL BEHAVIOR OF SOLIDS

O. D. Sherby, Professor, Materials Science and Engineering

Research Associates and Visiting Scientists:

G. Frommeyer
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NSF-MRL through CMR Thrust Program on Plasticity and Metal Working

Research Report:

(1) Mechanical Behavior of Particulate Composites

Graduate Students and Research Associates:

L. Eiselstein	Mu Yeh Wu	D. Yaney
J. Wadsworth	O. A. Ruano	

Technical Objective:

The program centers on the mechanical behavior of particulate composite materials, with special emphasis on the influence of hard particles of the strength and ductility of polycrystalline metals.

Approach:

Techniques are being developed for the preparation of composite materials by powder metallurgy methods. Use is being made of a mechanical attritor for refining the mixing of powders prior to sintering and of a hydrostatic extrusion press for mechanical working difficult to shape particulate composites. A thermal cycling apparatus has been developed. The mechanical behavior of solids are being assessed by means of constant strain rate and constant stress creep tests. The elastic behavior of the composite materials is also being studied.

Progress:

Our research on large volume fraction composites has yielded new phenomena not previously reported. At low temperatures ($< 0.35 T_m$) particles contribute to strengthening mostly through grain size refinement and partially through dispersion strengthening per se. At intermediate temperatures ($0.35-0.6 T_m$) particles can contribute to dispersion ductilizing when particles become active sources of dislocations and vacancies; this situation leads to high strain rate sensitivity, a factor that enhances tensile ductility. At high temperatures ($< 0.6 T_m$) the large volume fraction composites exhibit strain aging and yield point effects with accompanying high strengths. In addition, a "threshold stress" appears to exist below which plastic flow apparently does not occur. Physical models to explain these effects are currently being developed.

An investigation has been initiated by Mu Yeh Wu on the development of internal stress superplasticity by thermal cycling of large volume fraction composite materials. Zinc-alumina composites have been chosen since composites have been studied extensively for their high temperature mechanical properties. These are particularly suitable materials because they exhibit threshold stresses below which no creep will occur. Our ideas would suggest that such materials will not only creep below the threshold stress, under thermal cycling conditions, but more importantly, they will creep superplastically. Such results, if verified, can lead to new processing techniques for materials which normally are considered difficult to form at elevated temperature. Thermal cycling experiments have been devised to evaluate the influence of heating-and-

cooling rates, temperature range and applied stress on the plasticity of zinc-alumina composites.

The ease of deformation of superplastic materials would suggest that such materials, when in powder form, can be densified by pressing at intermediate temperatures. We are investigating the warm pressing characteristics of such materials; results by Caligiuri and Sherby on UHC steel powders indicate that higher densifications result when powders are warm pressed under superplastic conditions than under non-superplastic conditions.

Eiselstein, Ruano and Sherby are studying the structure and properties of rapidly solidified white cast iron powders. These powders were prepared by Pratt and Whitney, Florida, by their RSR (rapid-solidification-rate) process. The as-quenched structure is one consisting principally of retained austenite with ledeburite (mixture of carbides and retained austenite) and some martensite. After intermediate temperature annealing this structure changes to one consisting of a matrix of ferrite containing fine carbides. The mechanical properties of these RSR white cast iron powders (2.4 to 3%C) after densification at 650°C are being investigated. The results are impressive. Whereas ordinary (unalloyed) white cast iron is totally brittle in tension at room temperature, the compacted RSR white cast iron powders exhibit 5% tensile ductility. In compression tests at room temperature, the rapidly solidified white cast irons exhibit 25% strain prior to failure in contrast to only 5% strain in ordinary white cast irons. In addition, they are superplastic at intermediate temperatures (1000-1400% elongation) exhibiting no cavitation during deformation. These results suggest new methods of enhancing properties of high alloyed tool steels.

Ruano, Wadsworth and Sherby have shown that the densification of rapidly solidified white cast iron powders under stress can be enhanced by multiple phase transformations through thermal cycling. This enhancement occurs by accelerated creep flow during phase changes (transformation superplasticity). The stress range where transformation-assisted densification can occur is shown to be between 1.7 MPa (250 psi) and 34.5 MPa (5000 psi). Below 1.7 MPa insufficient strain occurs during phase transformation to cause significant densification

even after many transformation cycles. Above 34.5 MPa densification occurs principally by normal slip creep. These results indicate that high densification of ferrous base materials is possible at low applied external stresses by taking advantage of phase transformation superplasticity. In addition, if the transformation temperature is low, for example below 750°C, the ultrafine structures existing in the original powders can be retained in the densified compacts.

(2) Mechanical Behavior of Laminated Composites

Graduate Students and Research Associates

B. C. Snyder
W. Moberly

G. Frommeyer
D. W. Kum
J. Wadsworth

Technical Objective:

The program centers on the preparation of laminated composites of ultrahigh carbon (UHC) steel and mild steel, with special emphasis on a study of the mechanical properties of such composites at low and intermediate temperatures.

Approach:

Techniques for solid state bonding ultrahigh carbon steel to mild steel at intermediate temperatures are being developed utilizing superplastic microstructures. Tensile, impact, creep and bend tests are used to characterize and interpret mechanical properties.

Progress:

Ultrahigh carbon (UHC) steels, when in fine-grained form, can be readily solid-state welded to one another or to other ferrous materials. In fact, the ultrafine structure permits bonding at unexpectedly low temperatures, even below the A_1 temperature. It is believed this is due to the presence of many grain boundaries which accelerate the bonding process at adjoining interfaces. Itoh, Tokizane, Wadsworth and Sherby have shown that thick plates of monolithic 1% C UHC steel can be prepared by roll-bonding several thin sheets of the same material when in a fine grain condition. The low temperature of roll-bonding

(~ 650°C) assures retention of the fine grain size in the solid state bonded plate. Thus, massive samples can be made from UHC steels even when mechanical working facilities do not exist for preparing thick plate from large ingots. Standard charpy impact tests of the roll bonded material reveal a 60°C decrease in the D.B.T.T. of a 1%C steel by grain size refinement. B. C. Snyder, D. W. Kum and W. Moberly have prepared laminated composites of UHC steel bonded to mild steel in alternating layers, ranging from 3 to 360 layers. Such ferrous base composites are unique in at least three respects. First, the bond between the dissimilar steels is metallurgically perfect since ferrite of the UHC steel is bonded to the same composition ferrite of the mild steel. This means that it is very difficult to cause shear failure at the interfaces of the composite. Second, such laminated composites can be selectively heat treated. That is, heating to just above the critical temperature will transform the UHC steel but the mild steel remains unaffected. Upon quenching, a composite consisting of alternating layers of ultra-hard martensite and soft mild steel is created. The bond between the two constituents remains perfect and cannot be readily separated, thus leading to a high strength, high toughness composite. Third, the laminated composite can be superplastic at intermediate temperatures provided the strongest of the two constituents is superplastic. Snyder has shown that UHC steel laminated composites can exhibit 500% elongation at 650-700°C.

(3) Deformation of Materials at Warm and High Temperatures

Graduate Students and Research Associates:

T. Oyama	J. Wadsworth	S. M. deJesus
B. Snyder	O. Ruano	W. Avery

Technical Objectives:

To study the mechanism of deformation at high strain rate at warm and high temperature. Study of the mechanical behavior of unusual structures developed by thermal-mechanical processing operations with special emphasis in the warm working range of temperatures where subgrains and/or fine grains are developed.

Approach:

Constant strain rate tests and special thermal-mechanical processing treatments are used with the objective of developing ultrafine structures. A rapid quenching technique during high strain rate torsional deformation has been devised to assess the deformation mechanism of warm and hot working. Superplastic characteristics of fine grained materials are being studied by means of tension and compression testing.

- a) Development of controlled fine structures in ultrahigh carbon steels by thermal-mechanical processing. (Warm working and superplasticity)

We have been attempting to develop very fine grained structures in ultrahigh carbon (UHC) steels by special thermal-mechanical treatment (TMT) processing. Our research has centered on plain carbon steels containing 1.0 to 2.1% carbon (fifteen to thirty-two volume percent cementite respectively). Various TMT processing procedures have been developed which have resulted in particulate composites of cementite in iron containing ferrite grains finer than one micron in size. Such high carbon steels are superplastic at warm temperatures (elongations of over 1500% have been achieved). Furthermore, they can be made strong and ductile at room temperature. Ultrahigh carbon steels can be made more ductile than mild steel at room temperature. A patent has been issued to Stanford for the development of these fine grained UHC steels (U. S. Patent No. 3,951,697). In addition to exhibiting superplastic characteristics, the UHC steels can be heat treated to possess exceptionally high hardnesses (R_c 69 to 70). The fine martensite needles that form from the prior fine austenite grains lead to steels with compression fracture stresses exceeding 600,000 psi and compression ductility in the order of ten percent.

The development of ultrafine ferrite-cementite structures in the UHC steels has led to other unexpected results. Such fine-structure steels, when heated to just above the critical temperature to form austenite plus cementite, will exhibit a divorced eutectoid microstructure upon transformation cooling. Pearlite will not form; the fine interparticle spacing between cementite particles apparently

allows the dissolved carbon in austenite to precipitate on the pre-existing cementite during transformation. Oyama, Wadsworth and Sherby are investigating variables controlling formation of divorced eutectoid microstructures. This transformation can prove very useful in terms of ready attainment of desirable fine microstructures during TMT processing of UHC steels.

b) Mechanism of warm and hot working in crystalline solids

The factors influencing ductility and ductile fracture of materials at elevated temperature have not been studied extensively. Such studies are of paramount importance in assessing the formability of materials. A torsion apparatus has been developed at Stanford capable of deforming materials up to strain rates of 10,000 percent per second and temperatures of up to 2200°F. One of the unique features of our apparatus is that samples can be quenched instantaneously after deformation. In this manner the exact mechanism of plastic flow during high strain rate deformation can be evaluated. We are also capable of simulating complex thermal-mechanical processing operations with small scale samples.

Our work has revealed that structural change during warm working of polycrystalline solids is characterized by the formation of well defined subgrains. The subgrain size developed depends primarily on the modulus compensated stress, σ/E , and is insensitive to solid solution alloying, crystal structure and stacking fault energy. The nature of the subgrain boundary, however, appears to be a function of the temperature and strain at which it is formed. For a given subgrain size, the higher the temperature of working the more effective is the subgrain boundary as a barrier to low temperature plastic flow. We have shown that subgrains can be a more potent method of hardening than grains in the fine size range (ten microns and less). Preliminary results by us suggest that warm working has higher potential for low temperature hardening than cold working. Studies include austenitic and ferritic stainless steels as well as several iron base binary solid solution alloys. Schmidt, Klundt, Walser and Sherby are studying the influence of large plastic strain ($\epsilon = 15$ to 20) at warm temperature on the development, and nature, of subgrain boundaries. Results on a ferritic

stainless steel indicate that the misorientation angle of subgrain boundaries gradually increases with increasing strain; at strains as high as 15, the average misorientation angle is over twenty degrees. Similar results have been obtained after extensive warm working of a mild steel (0.2%C content).

c) Large strain deformation at warm temperatures (NSF/CMR Thrust Program on Plasticity and Metal Working of Materials)

Warm rolling is a promising technique for attainment of fine subgrain structures in crystalline solids. We have illustrated that mild steel can be strengthened considerably by warm rolling and the yield phenomenon can be eliminated. When large strains are imposed on plates at such temperatures, however, they can alligator or edge crack. These fractures are undesirable features of rolling. These defects are a result of residual stresses developed during rolling. To the best of our knowledge, no systematic studies have been performed to assess the factors leading to ductile fracture by alligatoring or edge cracking in metals during warm rolling. It is our purpose to investigate the variables that can contribute to such ductile failures.

Our newly acquired rolling equipment at Stanford will permit us to study the influence of the degree of deformation per pass, the temperature, and the time at temperature between passes. An additional important variable influencing the development of residual stresses is the microstructural state of the material considered. If a sample is ultrafine grained, it can exhibit a high degree of recovery during and after rolling which, in turn, can reduce residual stresses. Specifically, we are investigating the warm rolling characteristics of two steels. One is a mild steel (1020) with which we have had considerable experience. The other is an ultrahigh carbon steel containing fine grains. Both materials are being rolled in the temperature range of 500°C to 700°C. Preliminary studies have revealed that ultrahigh carbon steels alligator less readily than mild steel in the temperature range around 600°C. Current tests are planned to quantify the factors leading to the two principal defects observed in rolling - alligatoring and edge cracking.

d) Creep of polycrystalline solids

Our studies are directed at determining the contribution of subgrains and dislocations to the creep process. Using stress-change tests and change-in-strain-rate tests, it has been possible to determine the influence of strain rate on the flow stress at constant structure. Such tests also permit determination of the possible influence of subgrain size and/or dislocation density on the creep rate. Studies on pure aluminum, coupled with other data on high stacking fault energy materials, reveal that the creep rate can be given by:

$\dot{\epsilon} \approx 10^{11} \frac{D_{\text{eff}}}{b^2} [S] \left(\frac{\sigma}{E}\right)^8$. Here D_{eff} is the effective diffusion coefficient, S is a structure factor, σ is the creep stress, E is the dynamic unrelaxed elastic modulus and b is Burgers vector. The structure factor, S , is the form $\left[\left(\frac{\lambda}{b}\right)^{\rho} \left(\frac{160}{2}\right)^{3-\rho}\right]$ where λ is the subgrain size and ρ is the dislocation density. There are no contemporary creep theories that can explain the eight power dependence of creep at constant structure. This is an important area for further theoretical creep modelling. Kassner, Miller and Sherby are currently attempting to separate the influence of dislocation density and subgrain size on the creep rate. Lin and Sherby have extended the application of the constant structure creep relation to oxide dispersion strengthened (ODS) materials by including a threshold stress. Excellent quantitative predictions of the creep behavior of ODS alloys are possible with this modified relation. Clements and Sherby are investigating the creep of polyethylene and examining the possible applicability of phenomenological relations given above for metals to crystalline polymers such as polyethylene.

White, Oyama, Wadsworth and Sherby have examined the superplastic behavior of all fine grained superplastic materials reported in the literature. These studies are intended to assess the phenomenology of superplastic flow and to elucidate the mechanisms and rate controlling processes taking place during such deformation. A quantitative relation has been developed which describes well the temperature, stress and grain size dependence of the superplastic creep rate, $\dot{\epsilon}_{\text{spf}}$, of fine grained materials. This is given by the relation:

$$\dot{\epsilon}_{\text{spf}} = 2 \cdot 10^9 \frac{D_{\text{eff}}}{b^2} \left(\frac{b}{d}\right)^2 \left(\frac{\sigma}{E}\right)^2$$

In this relation $D_{\text{eff}}^x = D_L + 0.01 D_{\text{gb}} f_{\text{gb}}$ where D_L is the lattice diffusion coefficient, D_{gb} is the grain boundary diffusion coefficient and f_{gb} is the fraction of atoms in a given material associated with grain boundaries. The term f_{gb} is generally given as $2\pi b/d$ where b is the Burgers vector and d is the grain size. This relation predicts that at low temperatures and fine grain sizes (in the range where superplasticity is observed) the creep rate is given by $\dot{\epsilon}_{\text{spf}} \propto D_{\text{gb}} \left(\frac{\sigma}{E}\right)^2 \left(\frac{b}{d}\right)^3$ and at high temperatures and coarse grain sizes, $\dot{\epsilon}_{\text{spf}} \propto D_L \left(\frac{\sigma}{E}\right)^2 \left(\frac{b}{d}\right)^2$.

This predicted temperature, stress and grain size dependence is in close agreement with experimentally observed behavior. The phenomenological relations developed permit predicting quantitatively the factors which can extend the range over which superplastic flow can dominate the deformation process. Such knowledge is of great importance industrially, for economic feasibility of superplastic forming depends on enhancing the rate at which such processes can occur. Additional current studies on superplastic flow mechanisms center on the importance of size and hardness of second phase, the nature of the grain boundary (i.e. the misorientation angle) and the ease of grain boundary and interphase boundary sliding and separation.

Ruano and Sherby have shown that grain boundary sliding (g.b.s.) as a deformation mechanism is generally more important than diffusional processes (Coble Creep) at intermediate temperatures and low stresses. This interpretation eliminates the need for a threshold stress which must be introduced when Coble creep is assumed to be rate-controlling. In a related study, Ruano, Miller and Sherby consider the contribution of dislocation short circuit pipe diffusion to grain boundary sliding when the lattice diffusion coefficient is the rate-controlling process in g.b.s. This consideration predicts an influence of grain size on the creep rate ($\dot{\epsilon} \propto d^{-2}$) in the stress range where the stress exponent, n , is equal to 4, an experimental finding which, prior to this study, was considered to be an anomalous observation.

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1. "Creep of Oxide Dispersion Strengthened Materials (with Special Reference to T-D Nichrome", (with J. H. Lin), in press, Res. Mechanica (1981).
2. "Principles of Superplasticity and its Application", (with R. Caligiuri, E. Kayali and R. White), Advances in Metal Processing, Proceedings of the Twenty-Fifth Sagamore Conference, Plenum Press, 1981.
3. "On the Bulat - Damascus Steels Revisited", (with Jeffrey Wadsworth), Progress in Materials Science, 25, 33-68 (1981).
4. "Superplasticity - Prerequisites and Phenomenology" (with J. Wadsworth and T. Oyama), Advances in Materials Technology in the Americas, Vol. 2, Materials Processing and Performance, 1980, ASME, New York, 29-41.
5. "Manufacture and Mechanical Properties of Laminated and Monolithic Fine-Grained High-Carbon Superplastic Bearing Steel" (with T. Itoh, M. Tokizane and J. Wadsworth), Journal of Mechanical Working Technology, 1981, in press.
6. "Superplasticity in a Tool Steel" (with J. Wadsworth and J. Lin), Metals Technology, 1981, in press.
7. "Damascus Steel Rediscovered", by Oleg D. Sherby, Tetsu to Hagane (J. Iron and Steel Inst., Japan) in Japanese, 66, 114-124 (1980).
8. "Grain Refinement and Superplastic Behavior in a Commercial Bearing Steel"(with Motohiro Okade and Masaharu Tokizane), accepted for publication in Transactions, Iron and Steel Institute of Japan, 1981.
9. "Ductility Improvement of a Low-Carbon Steel by Warm Rolling and Annealing" (with D. L. Bourell), Metallurgical Transactions, 12A, 140-142 (1981).
10. "The Influence of Pipe Diffusion on Creep of Fine Grain Materials", (with O. A. Ruano and A. K. Miller) accepted for publication in Materials Science and Engineering, 1981.
11. "Subgrain Strengthening Revisited", (with Alan K. Miller and Michael E. Kassner), Metals Forum, Journal of the Australasian Institute of Metals, 1981, in press.
12. "Superplasticity-Prerequisites and Phenomenology", keynote lecture presented at Sixth Inter American Conference on Materials Technology, August 13, 1980, San Francisco, California.
13. "Ultrahigh Carbon Steel and Ultrahigh Carbon Steel Composites", talk given by Oleg D. Sherby to Bethlehem Steel Research Laboratory,

Bethlehem, PA (October 38, 1980), Lawrence Livermore National Laboratory (May 19, 1981), Army Materials and Mechanics Research Center, Watertown, MA (June 15, 1981), ARADCOM Headquarters, Dover, N.J. (June 18, 1981) and Ballistics Research Laboratory, Aberdeen Proving Grounds, Maryland (June 19, 1981).

14. "Superplasticity: Prerequisites, Phenomenology and Applications", talk given by Oleg D. Sherby to Westinghouse Research Laboratory, Monroeville, PA (October 29, 1980), to NATO Structural Materials Conference, Bremen, Germany (April 9, 1981), to General Motors Research Center, Warren, Michigan (June 10, 1981), and to International Harvester Corporate Research Center, Chicago, Ill. (July 15, 1981).
15. "Examples of Metal-forming Defects at Finite Deformation", talk by Oleg D. Sherby, given at research workshop on plasticity of metals and computation, Stanford University (June 29, 1981).
16. "Intermediate and High Temperature Creep of Polycrystalline Sodium Chloride". keynote talk presented by Oleg D. Sherby at conference on sodium chloride, Sandia Laboratories, Albuquerque, New Mexico, April 29, 0, 1981.
17. "Enhanced Densification of White Cast Iron Powders by Cyclic Phase Transformations under Stress" (with Oscar Ruano and Jeffrey Wadsworth), submitted for publication.
18. "The Yield-Point Suppression in Warm-Rolled Mild Steel", talk by D. Bourell at Fall Meeting, AIME, Pittsburgh, PA, October 5-9, 1980.
19. "Divorced Eutectoid Transformations in Ultrahigh Carbon Steels", talk by T. Oyama at Western Metals Congress and Exposition, ASM, Los Angeles, CA, March 26, 1981.

53. MICROSTRUCTURAL ASSESSMENT BY ACOUSTIC METHODS

J. C. Shyne, Professor, Materials Science and Engineering

Graduate Student:

N. Grayeli (Received PhD during report period.)

Agency Support:

An Associated Program, AFOSR F49620-0217

Technical Objective:

To develop nondestructive acoustic methods for assessing the microstructure and microstructure-related properties of materials. To establish the dependence of acoustic properties of solids upon their microstructural features.

Approach:

Acoustic signals in the 1 to 50 MHz range are used. Only bulk compression waves have been used; however, future work will include shear and Rayleigh waves. The velocity and attenuation of acoustic signals transmitted through solids are correlated with microstructural features.

Research Report:

1. Velocity variations in a steel object or velocity comparisons between steel specimens of identical composition can be usefully related to microstructure. For example, end quench hardenability test specimens of a variety of hardenable alloy steels were surveyed using acoustic velocity with comparable precision as for conventional hardness surveys.
2. Acoustic velocity was used to detect preferred crystal texturing. The spatial variation of the weak fiber texture in a rolled bar of 304 stainless steel was revealed by acoustic velocity measurements in agreement with conventional X-ray diffraction measurements.

3. The attenuation of acoustic signals in pure copper specimens was quantitatively correlated with grain size measured metallographically. Attenuation was caused by mixed stochastic and Rayleigh grain scattering, and the practical possibility for acoustic grain size measurement was demonstrated.
4. Acoustic attenuation in plain carbon steel specimens depended upon the proportions of pearlite and ferrite, with maximum attenuation occurring with nearly equal amounts of pearlite and ferrite. This is predicted by a grain scattering attenuation theory for mixtures of grains of different crystal phases. The colonies of lamellar pearlite were treated as crystallites with hexagonal elastic symmetry.
5. The acoustoelastic effect (dependence of velocity on the static stress state) was observed to vary with position in a stainless steel bar. The acoustoelastic variations appeared to be caused by the variations in preferred crystal texture measured in the same steel.

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2. J. C. Shyne, N. Grayeli, and G. S. Kino, "Acoustic Properties as Microstructure Dependent Materials Properties," Proceedings of Symposium on Nondestructive Testing, A.I.M.E. (in press).
3. N. Grayeli, F. Stanke, G. S. Kino, and J. C. Shyne, "Effect of Grain Size and Preferred Crystal Texture on Acoustic Properties of 304 Stainless Steel," Proceedings of 1980 Review of Progress in Quantitative NDE (in press).
4. N. Grayeli, "Acoustic Nondestructive Evaluation of Microstructure," (Ph.D Thesis) Stanford University, June 1981.

54. LASER MEASUREMENTS OF PHOTOVOLTAIC PROPERTIES

A. E. Siegman, Professor, Electrical Engineering

Graduate Student:

Philippe M. Fauchet

Agency Support:

DOE-DE-AT03-66ER10101

Technical Objective:

To make real time in situ measurements of physical processes during annealing of semiconductors by ultrashort laser pulses; to use these data both to model the physics behind laser-induced phase transformations, and to design and test novel experimental techniques that will lead to improved efficiency or unique applications.

Research Report:

We have performed a series of experiments on ion-implanted layers of Si and GaAs. The threshold for annealing with picosecond pulses has been accurately determined. We have also completed a detailed experimental study of surface structures associated with annealing by nanosecond and picosecond pulses, at 1.06 μm and 532 nm.

A theoretical study is under way.

We are completing a study in which a transient grating of carriers induced by two laser pulses coincident in time and space at the surface of the sample creates a permanent grating pattern formed of alternating annealed and non-annealed strips. This technique is applicable only for a specific range of wavelength and pulse duration.

We are now starting the study of thin ($\approx 1 \mu\text{m}$) films of polycrystalline silicon on quartz. We are planning to perform several

two-pulse experiments, where one picosecond pulse can be delayed with respect to the other. Such real-time measurements will contribute to improving the understanding of the physics behind ultrafast heating and cooling, melting and other phase transformations, and may lead to significant technological advances.

55. PICOSECOND SPECTROSCOPY USING A PHOTOACOUSTIC DETECTOR

A.E. Siegman, Professor, Electrical Engineering

Research Assistants:

J.M. Heritier
J.E. Fouquet

Agency Support:

AFOSR 80-0145
NASA NGL-05-020-103
NASA NSG-7619

Technical Objective:

To demonstrate and use the capability of photo acoustics as a detection mean in picosecond spectroscopy measurements.

Research Report:

We have developed a new photoacoustic cell (Fig. 1) in the form of an elliptical cylinder, in which the acoustic impulse generated by a laser beam is focused onto a piezoelectric transducer. The resonances of the cell and of the transducer have been investigated and are well understood. The very clean impulse response of the cell makes it useful in pulsed photoacoustic experiments.

Our longer-term objective in the work reported here is to measure excited-state relaxation times for atoms and molecules in the subnanosecond to picosecond range, as well as optical saturation and multiphoton effects in gases and liquids, by combining the techniques of picosecond optical spectroscopy with photoacoustic (rather than optical or fluorescent) detection. We propose, for example, to measure excited state lifetimes by passing pairs of picosecond optical pulses (at the same or two different wavelengths) through a sample to excite a photoacoustic response. We expect to see a change in the amplitude of this

response, averaged over several repeated pulses, as the time delay between the two optical pulses is varied in the picosecond to nanosecond range. We believe that techniques of this type have great potential utility for picosecond spectroscopy in highly dilute, weakly absorbing or nonfluorescing molecular systems, such as liquid suspensions of biological molecules. Applications to time-resolved photoacoustic spectroscopy in gases also appear feasible.

Reference Publications:

1. J.M. Heritier, J.E. Fouquet, K. Jackson and A.E. Siegman, "Picosecond Photoacoustics Using an Elliptical Acoustic Cell," to be presented at the Second International Topical Meeting on Photoacoustic Spectroscopy, Berkeley, California, June 22-25, 1981.
2. J.M. Heritier, J.E. Fouquet and A.E. Siegman, "Photoacoustic Cell Using Elliptical Acoustic Focusing," submitted to Optics Letters.

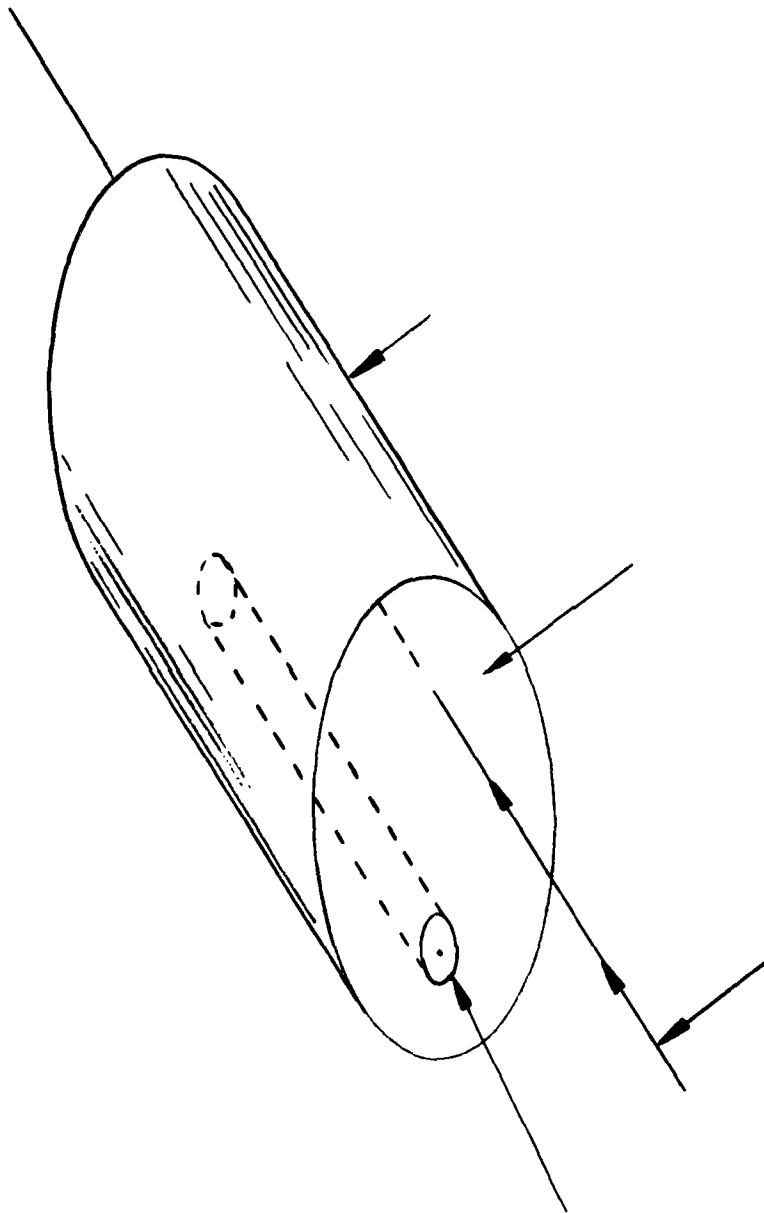


Fig. 1: Opto-acoustic sample cell. By passing the laser beam along one focal line of an elliptical cylinder, it is possible to focus all the optically generated acoustic signal onto a thin piezoelectric cylinder located on the opposite focal line, thus greatly enhancing the peak opto-acoustic signal.

56. MEASUREMENT OF ULTRAFAST PHENOMENA

A. E. Siegman, Professor, Electrical Engineering

Graduate Student:

F. P. Trebino

Agency Support:

N00014-75-C-0632

Technical Objectives:

To measure ultrashort lifetimes of atomic and molecular excited states.

Approach:

To employ a "tunable transient-grating" light scattering technique similar, in principle, to the transient-grating technique, but which does not require the use of ultrashort pulses.

Research Report:

In the past few years, our group has successfully measured ultrashort molecular lifetimes with a "transient grating" technique [1] in which two picosecond pulses from the same laser arrive at an experimental sample coincident in time, but from slightly different directions, producing a transient hologram pattern or grating of excited states. By measuring the diffracted intensity of a variable delay laser probe pulse (averaged over many pulses) as a function of the delay between excitation and probe pulses, one can measure the photo-excited state decay time with a resolution of approximately the laser pulsewidth. This method has been used successfully to measure relaxation times from 10^{-8} to 10^{-11} second, a resolution unobtainable using conventional optical detectors, and measurement methods.

The tunable transient-grating technique [2] is similar in principle to the transient grating technique, but does not require the use of ultrashort pulses and has potential time resolution approaching the

femtosecond range. Two frequency-tunable Q-switched laser pulses are allowed to interfere in an experimental sample producing a moving grating of excited states. The diffracted intensity of a simultaneously incident probe pulse of appropriate wavelength is then measured as a function of the grating velocity or frequency difference between the two exciting laser beams. Break points in this curve determine the excited decay time.

We have studied various beam geometries for use in this technique [3] and we have constructed the necessary apparatus to demonstrate the tunable transient grating technique, which consists of three tunable dye lasers [4] to produce the two excitation pulses and the probe pulse, and a Q-switched Nd:YAG laser whose output beam is frequency-doubled and split to pump the three dye lasers. We are at present preparing to demonstrate the techniques on samples consisting of laser dyes - molecular systems known to have excited states with ultrashort lifetimes. Once these initial experiments are completed, a computer-interfaced detection system will be constructed and other molecular systems, such as semiconductors, organic molecules, and saturable absorbers will be studied.

Reference Publications:

1. Donald W. Phillion, Dirk J. Kuizenga, and A. E. Siegman, "Subnanosecond Relaxation Time Measurements Using a Transient Induced Grating Method," Appl. Phys. Lett. 27, 85-87 (1975).
2. A. E. Siegman, "Proposed Picosecond Excited-State Measurements Method Using a Tunable-Laser-Induced Grating," Appl. Phys. Lett. 30, 21-23 (1977).
3. R. Trebino, James P. Roller, and A. E. Siegman, "Beam Geometries in Non-degenerate Four-Wave Mixing and Induced Grating Experiments," to be published.
4. R. Trebino, James P. Roller, and A. E. Siegman, "The Cassegrain and Other Beam Expanders in Higher Power Pulsed Dye Lasers," to be published.

57. STUDIES OF SURFACES AND INTERFACES IN SILICON BASED MATERIALS BY TEM AND AES

R. Sinclair, Associate Professor, Materials Science and Engineering
C. R. Helms, Adjunct Professor, Electrical Engineering

Graduate Students:

J. C. Bravman (Received MS during report period.)
R. W. Barton

Agency Support:

NSF/MRL Through CMR

Technical Objective:

To determine the structure and segregation effects of dopants at interfaces and grain boundaries in silicon based materials.

Approach:

Auger Electron Spectroscopy and Transmission Electron Microscopy are being used to study, at high resolution, the structural and chemical details of the Silicon-Silicon Dioxide interface and the grain boundary regions in polycrystalline silicon.

Research Report:

1. Material Preparation and Auger Electron Spectroscopy

Several studies of the phosphorus distribution in thermally oxidized silicon using Auger spectroscopy have already been completed and reported in the literature (1,2). These studies, which demonstrated the tendency of phosphorus to collect near (within 0.3nm) the Si-SiO₂ interface, have been used as a guide for the preparation of materials in this study. Using facilities in Stanford's Integrated Circuits Laboratory, silicon samples have been prepared with various bulk doping levels and then oxidized in a manner which maximizes the concentration

of segregated dopants. Phosphorus distributions in these samples were then determined with the Auger technique.

With a bulk doping level of up to $2.1 \times 10^{20} \text{ cm}^{-3}$, a peak interface value of $1.7 \times 10^{21} \text{ cm}^{-3}$ has been reached. As this represents about 3% of the bulk silicon lattice site density, the known solubility limit of phosphorus in silicon has clearly been exceeded. If one assumes that all the segregated phosphorus is held in one atomic layer, then there would be enough phosphorus to account for about 50% of this layer.

2. Transmission Electron Microscopy

A significant amount of work has gone into the development of a reliable technique for making cross-sectional TEM specimens from which micrographs can be taken at the ultimate resolution of our microscope, which is about 0.3 nm. It cannot be overemphasized how critically important such a technique is to our efforts. An earlier method, described in last year's report, has been dropped, due to its high failure rate. The new procedure is as follows. Six rectangular pieces of silicon (1mm x 10mm x .5mm) are bonded together on their flat sides using an especially strong thermosetting glue. From this composite, the standard 3mm dies are cut out, now being 1mm thick. These are mechanically polished to 0.01mm, and thinned in the ion beam miller to electron transparency. The specimens that allow high resolution pictures to be taken are extremely fragile, so some failures still occur. Nonetheless, the ability to fabricate these specimens represents a significant step forward in our research and gives us a capability which many other electron microscopy facilities lack. Additionally, its applicability extends to projects other than our own.

In our work, no fine scale precipitates of phosphorous have yet been found, even though, as noted above, our AES work indicates that the solubility limit of phosphorous in silicon has been exceeded. This seems to indicate that the phosphorous segregated to the interface is evenly distributed in a very narrow region, perhaps a monolayer. Further, the morphology is no different than that of silicon-silica interfaces in lightly doped materials, oxidized at higher temperatures, seen by other workers (3) and us. This apparently demonstrates that doping levels in silicon do not affect the structural aspects of its

thermally grown oxide interface.

Lastly, we have as yet no evidence for the formation of any crystalline phases in the near interface SiO_2 , as proposed in the theoretical work of Tiller (4).

Doped polycrystalline silicon is utilized in many technologically important areas, particularly as "interconnects" on integrated circuits and in low cost photovoltaic solar cells. One property of this system is a lower conductivity than that of similarly doped single crystal silicon. Two models have been proposed to explain this (5). The first has the dopant atoms moving to a grain boundary where they are electrically inactive. The second suggests that the dopant remains evenly distributed while the free carriers are trapped at these boundaries, also becoming inactive.

Recent work done on arsenic doped polysilicon, using ion backscattering spectroscopy, was interpreted in terms of the first model (6). This technique, however, is an indirect one, suffering from essentially no lateral resolution. When used in the STEM (Scanning Transmission Electron Microscope) however, our EDAX (Energy Dispersive Analysis of X-rays) system can provide microchemical analysis with lateral resolutions on the order of 10 nm. By aligning a grain boundary parallel to the electron beam, it may be possible to record changes in local dopant densities due to segregation effects. The primary constraint is the sensitivity of the system, being about one atomic percent.

Our initial experiments have indicated the presence of excess arsenic at the grain boundaries also in agreement with the first model. However, these results were obtained at the ultimate resolution of the EDAX unit; more work will be required before any conclusive statements can be made.

3. Future Work

To extend our knowledge of the Si-SiO_2 interface, work will be performed on samples prepared under varying doping and oxidation conditions. In particular, we will seek those conditions, if they exist, which can lead to either the precipitation of dopants or the formation of crystalline phases in the SiO_2 .

Our work will also proceed in the study of grain boundary segregation of arsenic in polycrystalline silicon. We will seek a fundamental

understanding of the relationship between dopant concentration and conductivity.

Additionally, we will begin work on the oxidation of polycrystalline silicon, a process of great technological importance. To develop a comprehensive model for the kinetics of this process, the effects of varying dopant levels, process temperatures, substrate materials, and thicknesses of poly-Si, plus the effects of the presence of grain boundaries, need to be investigated.

References

1. S. A. Schwarz, R. W. Barton, C. P. Ho, and C. R. Helms; J. Electrochem. Soc. 128, 1101 (1981).
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3. O. L. Krivanck, D. C. Tsui, T. T. Sheng, and A. Kamgar; The Physics of SiO₂ and its Interfaces, S. T. Pantelides, ed. (1978).
4. W. A. Tiller, J. Electrochem. Soc. 128, 689 (1981).
5. M. M. Mandurah, K. C. Saraswat, C. R. Helms, and T. I. Kamins, J. Appl. Phys. 51, 5755 (1980).
6. B. Swaminathan, E. Demoulin, T. W. Sigmon, R. W. Dutton, and R. Reif, J. Electrochem. Soc. 127, 2227 (1980).

Journal Publications (refereed)

1. "A Quantitative Assessment of the Capabilities of 2 1/2D Microscopy for Analyzing Crystalline Solids", G. M. Michal and R. Sinclair, Phil. Mag. A42, 691-704 (1980).
2. "Metallurgical Applications of the 2 1/2D TEM Technique", R. Sinclair, G. M. Michal and T. Yamashita, Met. Trans. A., in press.
3. "Observations of Atomic Motion on the Surface of a Cadmium Telluride Single Crystal", R. Sinclair, T. Yamashita and F. A. Ponce, Nature, 290, 386-388 (1981).
4. "The Structure of TiNi Martensite", G. M. Michal and R. Sinclair, Acta Cryst. B, in press.

5. "Room-Temperature Deformation Mechanisms and the Defect Structure of Tungsten Carbide", M. K. Hibbs, R. Sinclair, Acta Met. in press.
6. "Characterization of the Lattice Displacement Waves in Premartensitic TiNi", G. M. Michal, P. Moine and R. Sinclair, Acta Met. in press.
7. "A Morphological Study of 'Premartensitic' Effects in TiNi", P. Moine, E. M. Michal and R. Sinclair, Acta Met. in press.

Conference Articles, Etc. (non-refereed)

1. "High Resolution Imaging of Cadmium Telluride", R. Sinclair, F. Ponce, T. Yamashita and P. Pirouz, Proc. 7th European Congress on Electron Microscopy, 312-313, (1980).
2. "Structure Imaging of Defects in Cadmium Telluride", F. Ponce, T. Yamashita and R. Sinclair, Proc. 38th Annual Conference EMSA, 320-321, (1980).
3. "A Transmission Electron Microscopical Investigation of Phase Transformation in TiNi", P. Moine, G. M. Michal and R. Sinclair, *ibid*, 340-341.
4. "Defect Structure of Deformed TiNi", M. K. Hibbs, and R. Sinclair, *ibid*, 216-217.
5. "Analytical Electron Microscopy of Ferroelectric BaTiO₃", M. L. McCartney and R. Sinclair, *ibid*, 364-365.
6. "Combined High Resolution and Analytical TEM Studies of Phase-Separated Alloys", C. K. Wu, A. F. Marshall, G. Thomas and R. Sinclair, *ibid*, pp. 176-177.
7. "Microstructural and Chemical Analyses of BaTiO₃ Dielectrics", M. L. McCartney, R. Sinclair and G. J. Ewell, Advance in Ceramics, edited by L. M. Levinson, Am. Cer. Soc. Columbus, OH, 204-214, (1981).
8. "Imaging of Defects in Cadmium Telluride Using High Resolution Transmission Electron Microscopy", F. A. Ponce, T. Yamashita, R. H. Bube, and R. Sinclair, in "Defects in Semiconductors", edited by J. Narayan and T. Y. Tan, Elsevier North-Holland, in press.
9. "High Resolution Transmission Electron Microscopy of Semiconductor Materials", R. Sinclair, F. A. Ponce, J. C. Bravman, T. Yamashita, and P. Pirouz, Proc. of 2nd Oxford Conf. on Microscopy of Semiconductor Materials, in press (1981).

58. SURFACE, INTERFACE, AND ELECTRONIC STUDIES GROUP

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Agency Support:

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Catalytic Materials)
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SERI RW-0-1181-1

Technical Objective:

To utilize and develop tools of electron spectroscopy to study the properties of surfaces and interfaces. Emphasis is placed on a balanced program for both metals and semiconductors in order to provide the students with a broad insight into current research activities in the field.

Approach:

Use capabilities of conventional laboratory sources and the Stanford Synchrotron Radiation Laboratory (SSRL) to obtain experimental results and to interpret these.

This group, together with students, moves freely from one subgrouping to another. The faculty has strong links with other departments and laboratories at Stanford: the Departments of Electrical Engineering, Applied Physics, Materials Science and Engineering, and Chemical Engineering; the Stanford Electronics Laboratories; the Integrated Circuits Laboratory; the Stanford Synchrotron Radiation Laboratory; and the Joint Stanford-NASA Ames Institute for Surface and Microstructure Studies. The students come from Electrical Engineering, Applied Physics, Materials Science and Engineering, and Physics. They have undergraduate backgrounds in chemistry and chemical engineering as well as the departments listed above. The work is structured to maximize the interaction between different disciplines. This is an outgrowth of the interdisciplinary concept which characterizes CMR.

Research Report:

(1) The Electronic Structure of PtCu Alloys

Graduate Students: M. L. Shek
P. M. Stefan

Faculty: W. E. Spicer
I. Lindau

Towards the goal of understanding the surface electronic structure of PtCu alloys, as well as their implications for surface segregation and chemisorption, we have carried out the following experiments since our last report: (A) a comparative study of the valence bands of the (111) and (110) faces of the $\text{Pt}_{0.98}\text{Cu}_{0.02}$, using $h\nu = 150 \text{ eV}$, at which Cu 3d emission dominates; (B) the interaction of CO with Pt-Cu valence states; (C) preliminary angle-resolved photoemission measurements on the valence band of $\text{Pt}_{0.98}\text{Cu}_{0.02}$ (110) and its changes upon CO chemisorption. As an offshoot of Experiment (B), the effects of CO on $\text{Pt}4f_{7/2}$ and $\text{Cu}2p_{3/2}$ core levels have also been explored (Experiment D).

Experiment A has confirmed our previous suggestion that a correlation exists between surface segregation on the one hand, and surface bonding and atomic coordination on the other. In the 3-4 Å of the surface region sampled by photoemission, the average Cu concentrations are $9.8 \pm 3.2\%$ and $4.4 \pm 1.5\%$ for the (110) and (111) alloy surfaces, respectively. Their Cu 3d-derived electronic "density of states" also reflect differences in Pt-Cu surface bonding.

Experiment D explores the effects of CO on the Pt 4f_{7/2} core levels (observed with $h\nu = 150$ eV) of Pt_{0.98}Cu_{0.02} (110) and Pt (111), and the effects of CO on the Cu 2p_{3/2} core level (observed with Al Kα X-ray photoemission) of Pt_{0.98}Cu_{0.02} (110) at about 170°K. Core level shifts towards higher binding energy are observed for both types of core levels. These shifts may be explained by an initial-state chemical shift as well as a final-state screening charge delocalized by the CO-metal bond.

Analysis of the data from Experiments B and C are still in progress.

This work was partially supported by NSF INT 78-07268.

(2) The Electronic Structure of PdAu Alloys and the Water Reaction on Pd and PdAu

Graduate Student: D. L. Weissman-Wenocur

Faculty: W. E. Spicer
I. Lindau

Since our last CMR report, the reaction between hydrogen and oxygen to form water has been studied on Pd (111) and Pd_{0.8}Au_{0.2} (111) single crystal surfaces under ultrahigh vacuum, using thermal desorption spectroscopy (TDS). Under the "pulsed exposure" conditions of this study, the Pd yielded a higher reaction probability than the Pd-Au, as high as 83% per incident hydrogen. In contrast, previous steady-state experiments at atmospheric pressure showed a reaction probability enhancement of ~ 50 on adding Au to Pd, with maximum efficiency of $\sim 10^{-5}$. In the present work, the addition of Au to Pd decreased the binding energy of oxygen to the surface. The activation energies for oxygen desorption from Pd (111) ranged from 59 Kcal/mole at low coverage to 40 Kcal/mole at saturation coverage. The corresponding quantities from Pd_{0.8}Au_{0.2} (111) varied between 55 Kcal/mole and 37 Kcal/mole. Moreover, the

addition of Au to Pd drastically reduced the oxygen coverage from 10^{-12} at saturation on Pd (111) to $2-3\%$ at near-saturation on $\text{Pd}_{0.8}\text{Au}_{0.2}$ (111). Therefore, a long-range or "ligand" effect on the Pd-O bond seemed to be in operation. There was another important effect observed in our low-pressure experiments, a second oxygen binding state was seen on the Pd only, after partial oxygen removal by hydrogen. Our findings lead to the proposal of reaction mechanisms which can reconcile the low-pressure and high-pressure studies and which may explain the unusual enhancement seen at high pressures.

(3) Fundamental Studies of Cermets

Visiting Scholar: J. I. Gittleman

Faculty: W. E. Spicer

Auger electron and photoelectron spectroscopic studies of Au-SiO_2 and $\text{Au-Al}_2\text{O}_3$ cermets have been made. The cermets are thin films consisting of small grains of gold, with mean diameters in the range 10 \AA to 100 \AA , dispersed in a matrix of the insulator. They are formed by co-sputtering the components of the cermet into an appropriate substrate. The principal purpose of the study was to determine the effect on the electron states in Au of the intimate contact between the matrix atoms and the surface atoms of the grains.

Although in some specimens about 70% of the atoms in a gold grain was in contact with matrix atoms, no changes in the valence band or the 4f core levels were observed other than effects due to grain size only. That is to say our results were the same as those reported for free standing, comparably sized gold grains.

The absence of chemical interaction with the matrix on the part of the Au atoms suggests an interesting extension of this work. Using an appropriate matrix, probably carbon or silicon, Au cermets will be formed on substrates cooled to a nominal temperature of 77°K . Electron spectrographic studies of the 5d and 4f electrons of the Au as a function of annealing should reveal the evolution of these states as the gold clusters grow from isolated atoms to the bulk.

This work was supported by NSF-DMR-80-01741.

(4) Photoemission Investigations on Si and Ge - d Metal Interfaces

Visiting Research Associate: G. Rossi

Italian Associates: Dr. I. Abbati, Prof. L. Braicovich
Faculty: W. E. Spicer and I. Lindau

(A) The Nature of the Chemical Bond Between Si and Pd

The behavior of Si-d metal junctions is dominated by the formation of interfacial reaction products, which in turn determine the formation of the Schottky barrier and its electrical properties.

Exploiting the tunable radiation at SSRL which allows the measurement of photoemission at the Cooper minimum for the metal 4d orbitals, we were able to describe on a direct experimental basis the characteristics of the Si-Pd bond and the different orbital contributions contained.

Cooper minimum photoemission permits one to obtain valence band EDCs of Si-d metal interfaces with emission from the metal p and d electrons and from the semiconductor sp states having the same order of magnitude. In fact, the EDCs taken at the conventional energies (21.2 eV, 40.8 eV) are dominated by the metal d emission, and no details of the substrate can be seen.

The main features of the density of states at the Si (111)-Pd interface are, from greatest to least binding energy:

- (i) A deep s silicon structure little involved in the bonding, with some sp contribution from the metal around 11 eV below the Fermi level.
- (ii) A region of mixed orbitals (p from Si and d from Pd).
- (iii) A main structure around - 3 eV due to Pd d electrons.
- (iv) A region extending up to E_f of mixed orbitals (p from Si and d from the metal) of antibonding character.

The main features in the bonding are due to the rehybridization of the Si p and metal d electrons that form structures in the DOS similar to those known for bulk stoichiometric silicides. This configuration of the bond is reached at coverages smaller than one monolayer and is stable, at RT, for higher metal coverages. The new energy distribution of the silicon states is due to the breaking of the tetrahedral coordination typical of the diamond structure when the interface compound is

formed. In fact, the two EDC structures due to the sp^3 coordination of clean Si are lost at low coverages, being replaced by the new EDC peak referred to in (i).

This scheme of interpretation of the Si-d metal bond has been obtained by analyzing Si-Pd and Si-Pt data at RT and seems to be of general value for related interfaces.

Reference Publications:

1. G. Rossi, I. Abbati, L. Braicovich, I. Lindau, and W. E. Spicer, Solid State Comm., (submitted for publication).

(B) The Si/Pd Interface at RT, Studied by Energy Dependent SR Photoemission

An extensive study of the Si/Pd interface at RT has been carried out by means of energy dependent photoemission with the Cooper minimum method. Besides a confirmation of the general features of the bond between Si and Pd, we were able to follow the growth of the interface vs. coverage. The valence band EDCs at $h\nu = 80$ eV (full d contribution) and at $h\nu = 130$ eV (Cooper minimum for Pd 4d) show a constant evolution from a Si-rich mixed phase towards a metal rich mixed phase, but never reaching the valence band shape of the pure metal, within the interval of coverages explored (up to $\theta = 23$ ml). These features and the Si 2p core line intensity profile give the evidence of a graded reacted interface in which the silicon atoms are mostly coordinated with Pd atoms, and are not very sensitive to the details of the structure of the mixed phase. The analysis of the Si 2p core lineshape also gives interesting indications on the metal-rich surrounding of the Si-atoms; in fact, it presents the typical skewed lineshape of the metallic core lines due to the Sunjic-Doniach mechanism with contributions due to low energy losses.

Reference Publications:

1. I. Abbati, G. Rossi, L. Braicovich, I. Lindau, and W. E. Spicer, Proceedings of the PCSI 8 Conference, J. Vac. Sci. Technol. (in press).

(C) Thermal Accumulation of Si at the Si (111)-Pd Interface

Thermally induced Si accumulation onto Pd_2Si surfaces has been studied for the first time with synchrotron radiation photoemission.

Making use of the Cooper minimum EDCs and Si 2p core line spectroscopy of a Si (111) + 4 ml of Pd interfaces, thermally treated at increasing temperatures in the range 300°K to 700°K, we were able to see that a significant accumulation of Si on the top layers of the interface is obtained for temperatures higher than 550°K. In this Si-rich region, new bonding features between Si and Pd appear with respect to the RT (300°K) case. The new bond formation gives a substantial contribution to the driving force responsible for the thermally activated accumulation of Si; the Si-rich side of the interface has very stable bonds and this gives the first spectroscopic explanation of the stability observed for the Si-Pd interfaces prepared by annealing in device technology.

Reference Publications:

1. I. Abbati, G. Rossi, L. Braicovich, I. Lindau, W. E. Spicer, and B. De Michelis, Appl. Phys. Lett. (submitted for publication).

(D) The Si (111)/Pt Interface at RT

The growth of the Si (111)/Pt interface at RT has been studied in great detail with energy dependent photoemission spectroscopy. Making use of the Cooper minimum method, we were able to follow the modifications in the valence band density of states from the very beginning of the interface formation (i.e., for coverages starting at $\theta = 0.01$ monolayers) where the Si (111) disruption is observed, up to a metal rich situation ($\theta = 40$ ml). Three main regions have been identified in the interface. At very low, submonolayer, coverages ($\theta = 0.3$ ml), the Pt has the effect of destroying the surface and dramatically changing the Si (111) density of valence states, even before that evidence of a chemical reaction is seen. In an intermediate region ($1 \text{ ml} < \theta < 10 \text{ ml}$), a silicide-like phase is formed with stable features, but showing a gradient of concentration of Pt from a PtSi-like situation to a Pt₂Si-like situation. The evidence of a chemical reaction is seen in the disruption of the tetrahedral coordination of the Si atoms, which is characterized by the replacement of the double peak structure at -11 eV and -7 eV below the Fermi level, with a single peak around -9.5 eV in the valence band density of states. The high degree of intermixing taking

place from the very beginning of the interface growth is independently proved by the core line intensity profiles of Pt 4f and Si 2p. At higher coverages, a Pt enrichment is observed, but still the reaction is far from being saturated and the pure metal-like density of states is never reached in the coverage interval explored (i.e., up to 40 ml). The new main features of the Si/Pt valence band are due to a rehybridization of the sp states of Si and the 5d states of Pt. Lineshape analysis of the Si 2p core lines were also used to probe the changes in the local environment of Si with increasing Pt concentration giving the picture of Si atoms mainly surrounded by Pt atoms.

Reference Publications:

1. G. Rossi, I. Abbati, L. Braicovich, I. Lindau, and W. E. Spicer (to be published).
2. G. Rossi, I. Abbati, L. Braicovich, and I. Lindau, Proceedings of the Physical Electronics Conference, Bozeman, Montana, July 1981.

(E) Valence Band SR Photoemission for Ge (111)/d-Metal Interfaces

The Ge/d metal interfaces have been studied for the first time by photoemission. Three different systems were examined: Ge/Pd and Ge/Ni at RT with coverages in the range of 0.5 ml to 15 ml and Ge/Ag with great detail in the low coverage region (0.03 ml to 10 ml). In the case of Ge (111) + Pd a broad, reacted, germanide-like phase is formed with similar features to the Si (111)/Pd interface. The coverage threshold for the reaction appears to be higher for the Ge/Pd system than for Si/Pd, which may be related to the different heat of formation of the respective compounds. In the Ge (111)/Ni case, an evolution of the valence band vs. coverage from a reacted situation to a metal rich situation is found, indicating a strong gradient of concentration; the interface is narrower than in the Ge/Pd case as deduced by the trends of the intensity of photoemission from the Ge 3d core lines. The third case is the Ge (111) + Ag interface where the intermixing takes place only in a few layers, and a bulk-like Ag growth is quickly gained onto the interface which is narrow, but not atomically abrupt. In the Ge/Ag case Cooper minimum spectra were taken showing a similar behavior of the high energy part of the semiconductor valence band EDC as seen in the

Si/transition metal interfaces; the breaking of the tetrahedral coordination leads to a new structure around 10 eV below the Fermi level.

This work was partially supported by DARPA-ONR N00014-79-C-0072.

Reference Publications:

1. G. Rossi, I. Abbati, L. Braicovich, I. Lindau, and W. E. Spicer (to be published).
2. G. Rossi, I. Abbati, L. Baricovich, I. Lindau, and W. E. Spicer, Proceedings of the Application of Surface Analysis Conference, Dayton, Ohio, June 1981.
3. G. Rossi, I. Abbati, L. Braicovich, I. Lindau, and W. E. Spicer (to be published).

(5) Production of Large (~1.1 eV) Schottky Barriers on n-Type GaAs (110)

Graduate Students: P. R. Skeath
C. Y. Su

Faculty: W. E. Spicer
I. Lindau

It has been demonstrated that the Schottky barrier height on GaAs (110) is essentially independent of the metal used when the metal is deposited in *vacuo* onto an atomically clean GaAs surface. A Schottky barrier produced with Au, however, seemed to produce an unusually large barrier on n-type GaAs. Further study has now revealed that Au pins the Fermi energy much closer to the valence band maximum than other metals on both n- and p-type GaAs. By observing the variation of barrier height vs. Au coverage, it has been concluded that Au must first form defects as do the other metals studied and then, at higher coverages ~ 1 ml penetrate into the semiconductor, and introducing new defect levels (acceptors) near the valence band maximum.² Future experiments are planned in which the temperature dependence of the barrier height will be studied.

This work was supported by DARPA-ONR N00014-79-C-0072 and ONR N00014-75-C-0289.

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(6) Models of Column 3 and 5 Elements on GaAs (110): Application to Molecular Beam Epitaxy

Graduate Students: P. R. Skeath
C. Y. Su

Faculty: W. E. Spicer
I. Lindau

A phenomenological model of the bonding of Column 3 metals to GaAs (110) surfaces has been developed, in which the interfacial bonds are mainly nondirectional in character. The column 5 elements, on the other hand, form directional, covalent bonds to GaAs (110).¹ The implications of these results for crystal growth have been examined from a chemical (tight-binding) point of view. One important result is that it is the column 5 element which establishes registry between a growing surface layer and the semiconductor. It is concluded that adsorbed column 3 atoms must find a binding site with more than one column 5 nearest neighbor before it can form directional bonds (i.e., stabilize in a lattice site), due to the necessity of hybridization.²

This work was supported by DARPA-ONR N00014-79-C-0072 and ONR N00014-75-C-0289.

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(7) The Interaction of Oxygen with Si (111) Surfaces

Graduate Students: C. Y. Su
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Faculty: W. E. Spicer
I. Lindau

It is well known that the Si (111) surface exhibits a 2×1 reconstruction after cleaving at room temperature, and transforms to a 7×7 reconstruction after annealing at elevated temperature ($> 200^\circ\text{C}$). Understanding the nature of these reconstructions is important in understanding the covalent bonding in Si. Direct determination of the structure of the 7×7 reconstruction has so far been prohibited because of its complexity. During this reporting period, we have attempted to distinguish

various models for the 7×7 reconstruction through detailed comparisons of the oxygen adsorption properties on the 2×1 and the 7×7 surfaces. Our results have shown unambiguous support for the defect type model of the 7×7 surface.^{1,2}

We have also made progress in understanding the room-temperature oxygen adsorption configuration on the Si (111) 2×1 surface. By examining the evolution of the chemical shifts in the Si-2p of oxygen-covered surfaces under heat treatments, we have eliminated many possibilities and have narrowed the choice to a few possible Si-O bonding configurations.³ These results suggest that more systematic studies of the annealing effects may be very important in understanding the Si-O bonding.

This work was supported by DARPA-ONR N00014-79-C-0072 and ONR N00014-75-C-0289.

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(8) Studies of Semiconductor Surfaces and Interfaces: Photoluminescence from GaAs and InP Surfaces

Graduate Student: S. J. Eglash

Professional Associate: R. Street (Xerox, Palo Alto Research Center)

Faculty: W. E. Spicer

This research only began during this period, will combine theoretical and experimental efforts in an investigation of the mechanisms by which excess carriers (electrons and holes) recombine in semiconductors. In particular, we will compare surface recombination at the (110) surfaces of GaAs and InP. Studies at Bell Labs¹ and Nippon Electric Corp.^{2,3} show that nonradiative recombination at bulk crystal defects and at oxidized sites cause failures in light emitting diodes (LED's) and solid

state lasers by releasing heat that drives additional oxidation and defect formation.

It has previously been shown that the photoluminescence from InP is affected by oxide formation and defects at the surface.^{4,5} Our group at Stanford has developed a fundamental model for defect electronic states at the surfaces and interfaces of GaAs, InP, and GaSb.⁶ We hope to interpret carrier recombination in these materials at dislocations in terms of the known energies of their surface defect states.

This work was supported by DARPA-ONR N00014-79-C-0072 and ONR N00014-75-C-0289.

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(9) Laser-Enhanced Oxidation of GaAs (110) Surfaces

Graduate Student: W. G. Petro

Faculty: W. E. Spicer

The use of laser radiation as a means of processing semiconductor materials (annealing, alloying, cleaning, etc.) has been a subject of considerable interest over the past decade. However, a detailed understanding of the mechanism of energy transfer from the laser to the solid remains a subject of debate. In this report, we present the results of experiments in which GaAs surfaces were exposed to molecular oxygen while being irradiated by a laser. Analysis of core-level and valence-band photoemission spectra show that the effect of the laser is not merely a heating of the semiconductor material.

The core-level data were taken at an incident photon energy of 100 eV and the photoemitted electron from the As-3d and Ga-3d levels

were energy-analyzed. Comparison of these spectra with previous work using both excited and unexcited oxygen at room temperature shows striking differences. There is no indication of a shifted As peak other than the one at a binding energy of 2.9 eV greater than that of the unshifted As 3d level, implying that excitation of the oxygen molecules by the laser is unlikely. However, the amplitude of the shifted As level is much greater at a given oxygen exposure with the laser than it is at the same oxygen exposure without the laser.

For the highest laser power used (1.75W), we observe equally large shifted and unshifted peak areas at an exposure of 10^7 L. Under normal oxidation conditions, shifted peak area becomes equal to the unshifted peak area at an exposure of 10^{12} L. Furthermore, this appears to be an upper limit to the amount of chemisorbed oxygen under normal conditions. With the laser, however, the shifted As signal continues to increase, reaching a value of about 2.9 times the area of the unshifted peak at an exposure of 10^9 L. This indicates that the oxygen molecule is able to break-up and bond to a greater number of sites on the surface during laser irradiation, due to the availability of free electrons excited from the valence to the conduction band. Similar behavior is seen in the valence band data, where the appearance of the oxygen 2p level at various oxygen exposures correlates with that of the shifted As-3d level.

This work was supported by DARPA-ONR N00014-79-C-0072 and ONR N00014-75-C-0289.

(10) Photoyield Measurements on the Diamond (111) Surface

Graduate Student: P. J. Jupiter

Faculty: W. E. Spicer

Photoyield measurements on the (111) surface of naturally occurring diamonds show that the photoelectric threshold occurs at the band-gap energy (5.5 eV). This proves the existence of an effective negative electron affinity in diamond. Work done by Brad B. Pate shows the true electron affinity at the surface to be positive but band bending is sufficient to result in an effective negative electron affinity.¹

Relative photoyield measurements on the diamond (111) surface has also uncovered structure at the photoelectric threshold, between 5.5 eV (diamond band-gap) and 6.5 eV. This structure appears as "bumps" in the relative photoyield. Spacings between these "bumps" range from 0.13 eV to 0.18 eV. As the sample temperature decreased, the structure was noticed to sharpen. Because of its shape and temperature dependence, this phenomena is believed to be associated with a phonon-electron coupling, but more definitive evidence is still needed. Further studies will include absorption measurements on thin diamonds (12μ) at various temperatures.

This work was supported by ARMY DAAG29-78-G-0130.

Reference Publications:

1. B. B. Pate, W. E. Spicer, T. Ohta, and I. Lindau, J. Vac. Sci. Technol. 17, 1087 (1980).

(11) Formation of Surface States on Diamond

Graduate Student: B. B. Pate

Faculty: W. E. Spicer
I. Lindau

Studies of the (111) surface of natural diamonds using photoemission electron spectroscopy (PES) and low energy electron diffraction (LEED) have revealed the existence of two distinct surface structures, each with characteristic atomic and electronic structure. The two structures are denoted by 1×1 and $2 \times 2/2 \times 1$ which reflect the atomic periodicity at the surface. (Note: At this time it is unknown if the so-called $2 \times 2/2 \times 1$ surface structure is a 2×2 or a 2×1 structure due to an ambiguity in the LEED diffraction pattern.)

We find that while theory would predict that the 1×1 surface atomic structure should be accompanied by an intrinsic band of filled surface states in the fundamental band gap, the PES experiments demonstrate an absence of such surface states. Such a result may be the result of hydrogenation of the diamond surface, thereby saturating the dangling bonds and preserving the bulk atomic periodicity. In the preliminary experiments in which photons are used to stimulate the desorption of adsorbate ions (in this case H^+), we have demonstrated the

existence of hydrogen on the 1×1 surface. Additional photon stimulated desorption (PSD) experiments are in process which may further clarify the dependence of the electronic structure of the 1×1 surface on hydrogen.

In contrast to the 1×1 surface, we find surface states on the $2 \times 2/2 \times 1$ surface structure of diamond (111). The $2 \times 2/2 \times 1$ surface is obtained by a high temperature (5 min., $\sim 950^\circ\text{C}$) anneal of the 1×1 surface. This band of surface states is found centered at an energy 1.4 eV below the valence band maximum, with a width of 1.8 eV FWHM. The emission intensity from the surface state band is consistent with the existence of one filled state per surface atom. A parallel study of diamond's more stable allotrope, graphite, indicates that the $2 \times 2/2 \times 1$ surface of the (111) face of diamond is electronically distinct from graphite.

This work was supported by ARMY DAAG29-78-G-0130.

Reference Publications:

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(12) Surface Properties of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

Graduate Student: J. Silberman

Faculty: P. Morgen
W. E. Spicer
I. Lindau

The material $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ holds a large potential for infrared detection devices, due to its electronic properties.¹ These can be tailored to give optical absorption cutoff characteristics in the so-called "atmospheric window", by varying the composition, i.e., x . For use in devices, however, a better characterization of surface and interface properties of the material must be obtained. The present investigations will provide such information.

Of fundamental interest is the fact that these materials have unique properties, e.g., the highest known mobilities ($\sim 5 \times 10^6 \text{ cm}^2/\text{V-sec}$), quite different bonding energies for CdTe and HgTe, and very "weak"

mechanical properties. We suggest that all of these properties are related through the band structure. One objective will be to test this hypothesis, and, if correct, to work out the detailed connections, etc.

The surface composition and electronic structure have been measured with electron spectroscopic methods, including the use of synchrotron radiation (SSRL). For $x = 0.2, 0.31, 0.39$ and 1 (CdTe), we have obtained detailed information pertaining to the band structure at the surface, and the stability of the material. We find that surfaces prepared by cleavage under UHV are very stable with respect to loss of Hg.² These surfaces are also inert with respect to dry, neutral oxygen, but react with excited oxygen.²

The oxidation process is complicated in this ternary system. Thus sputter profiling of anodic oxides, 500 Å and 1000 Å thick, shows that the oxidation depletes the substrate of Hg, but the oxide layer itself contains hardly any Hg. The initial stages of interaction with excited oxygen were also found to decrease the surface concentration of Hg.

Other methods of surface preparation and cleaning have been, or will be, examined. Scraping and sputtering have been found to change the surface composition, which suggests that surface perfection is important in controlling the stability of the material.

Future studies are planned to address questions related more specifically to the surface order and microscopic concentrations, such as could be studied with LEED, and with synchrotron radiation with photon energies minimizing the escape depths of the highest lying core lines, i.e., Te 4d, Cd 4d and Hg 5d. Efforts will also be devoted to study epitaxially grown samples. For commercial devices, LPE will be the preferred method of growth. Thus studies of CdTe/Hg_{1-x}Cd_xTe heterojunctions and interfaces will be included in the future activities.

This work was supported by DARPA MDA 903-80-C-0496.

(13) Studies of C(ore) V(alence) V(alence) Auger Lineshapes

Visiting Scholar:	G. Rossi
Faculty:	P. Morgen
	W. E. Spicer
	I. Lindau

This study is a continuation of work done in Odense.⁵ There is presently a great deal of interest in determining the contribution to CVV Auger lineshapes from many-body effects, i.e., screening and relaxation. Here at Stanford, the $\text{Si}(L_{23}VV)$ line from Si/Pt interfaces is studied, in an attempt to correlate AES and UPS.⁵ Under a different project, photoemission from Si/Pt at the Cooper minimum has been used to get EDC's of Si at the interface. Auger data on the same system will be deconvoluted⁶ within different assumptions for the Auger matrix elements, and compared to the EDC's. The results may provide the desired information about many-body effects. The comparison between Auger data and UPS may also lead to the first direct experimental proof of the existence of Si-Pt hybridized states, in bulk PtSi or Pt_2Si and at the Si/Pt interface.⁷

This work was supported by DARPA-ONR N00014-79-C-0072.

(14) Studies of the Sputter Profiling Techniques

Graduate Student: J. Silberman
Faculty: P. Morgen
W. E. Spicer
I. Lindau
C. R. Helms

Sputter profiling⁸ is a very powerful technique to study the composition in depth of complex semiconductor and metal 3-dimensional devices, and the facilities here at Stanford are in heavy use for this purpose. However, there still exist at least two important problems in quantifying the resultant sputter profiles: (1) Preferential sputtering, and (2) calibration of the intensities of emitted electron lines (in AES or XPS) used to determine concentrations. The present efforts concentrate on establishing a body of experimental data which could help in gaining more insight into the two problems listed here. Thus a series of binary and ternary compounds, which are well characterized for composition and bulk structure, are sputter profiled with different experimental parameters, i.e., ion energy and primary electron beam energy. Several Auger and XPS lines are normally included in determining the concentration profiles in order to determine the homogeneity and effects

of different escape depths. We have already seen strong effects of inhomogeneity caused by preferential sputtering. Even after the sputter profiles have reached steady state, are inhomogeneous concentration profiles observed. With the present data on Si/C, Si/Mo, Zr/Cu, and Hg/Cd/Te, we conclude, in steady state, the surface layer is enriched in the compound with the highest sputter rate, while the bulk beneath the surface often is depleted of that component, due to diffusion enhanced by the ion beam. These findings would clearly question a lot of the procedures used in the past to obtain concentration profiles from the measured electron line intensities, as well as some of the assumptions normally underlying the use of SIMS. We hope to arrive at a more valid interpretation of the results of sputter profiling through the present and, probably, a number of future experiments.

This work was supported by DARPA MDA 903-79-C-0257.

(15) Studies of Thin Films of SiC_x

Graduate Student: K. Seaward

Senior Research Associate: T. W. Barbee, Jr. (Department of
Materials Science and Engineering)

Faculty: P. Morgen

As part of a project to investigate the fabrication of thin films of SiC_x ($x \approx 1$), sputter profiling and lineshape analysis of Si and C Auger lines of a number of samples were carried out. The results for preferential sputtering have already been included under (14) above, but after correcting for this, the concentrations found were in agreement with other techniques. For SiC_x , $x = 1.0$, the films are of the cubic β -SiC phase. Examination and deconvolution of the $\text{Si}(L_{23}VV)$ and $\text{C}(KVV)$ lines are performed in the light of band structure calculations with partial and local densities of states for Si and C atoms.⁹ The findings will contribute the same understandings as under (13) above. However, the fact that there are two lines in the spectrum that sample the valence electron distribution should make the interpretations more straightforward in this case.

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(16) Surface Induced Core-Level Binding Energy Shifts Measured With Photoemission Spectroscopy

Graduate Students: A. Viescas
M. H. Hecht

Faculty: I. Lindau

We have recently reported on intrinsic surface binding energy shifts observed in Yb metal. This work replicated the results of Alvarado, et al.,¹ who interpreted the shifted peaks, however, as a contaminant induced structure.

A simple model for calculating surface-bulk core level binding-energy shifts in metals was proposed by B. Johansson and N. Martensson.² This model predicts a value for these shifts of

$$\Delta E_c^{s,b} \sim 0.2[E_{coh}^{Z+1} - E_{coh}^Z - E_{Z+1}^{imp}(Z)]$$

where E_{coh}^Z is the cohesive energy needed to remove one atom from a solid with atomic number Z , and $E_{Z+1}^{imp}(Z)$ is the energy needed to dissolve (in the infinitely dilute case) a piece of $Z + 1$ metal into the Z metal.

The expected energy shift for polycrystalline Yb metal was thus calculated to be above 0.49 eV, in good agreement with the observed shift.

As a further test of this model, we have similarly calculated shifts for all of the transition metals, simple metals, and rare earth metals. We are currently planning photoemission experiments on several systems with predicted shifts large enough to be seen experimentally.

The importance of this model is its dependence on both surface and bulk coordination numbers. If we can establish the general validity of this model for polycrystalline systems, we can proceed to study particular crystal faces and reconstruction as well as surfaces of ordered compounds, using the magnitude of the bulk to surface shift as a probe of surface characteristics.

This work was partially supported by the NSF-MRL Program through CMR and NSF-DMR-79-13102.

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(17) Many-Electron Effects As Reflected in Partial Photoionization Cross Sections

Graduate Student: M. H. Hecht
Visiting Scholar: L. I. Johansson
Faculty: I. Lindau

The measurement of partial photoionization cross sections has two motivations: to shed light on the difficult theoretical problem of electronic photoexcitation in a many-bodied framework, and to determine essential physical constants needed for a variety of applications including photoemission spectroscopy of compounds, plasma diagnostics, and interpretation of astrophysical data. Accordingly, we have pursued this research on two fronts: the systematic replication of measurements of common elements, and the exploration of more exotic systems with excitations dominated by many-electron interactions.

Many-body perturbation theory predicts a broad, delayed onset of 4d excitation in 4d transition metal atoms as compared to the narrow, near threshold enhancement predicted by one-electron models. Our photoemission measurements of polycrystalline In, Ag, and Sb at the Stanford Synchrotron Radiation Laboratory (SSRL) confirmed these calculations, demonstrating also that this excitation is atomic-like in character.

In Ba, many-bodied calculations predict sharp enhancement of outer 5p and 5s shell emission accompanying a broad 4d photoabsorption line. Our measurements confirm the qualitative nature and the relative intensities of these enhancements, and in addition, disclose the nature of a two-electron discrete excitation 20 eV above the 4d threshold.

The relative intensities of the photoemission peaks of the spin-orbit split 5d levels of Pt, Au, and Pb exhibit modulations between 80 and 200 eV photon energy. We have determined that in Pb, modulations can be explained by atomic matrix element effects. In Pt and Au, however, band structure must be considered in a complete explanation of this phenomenon.

Most recently, we have performed absorption measurements at the 3d threshold (1000 - 1800 eV) of various rare earth materials using the new double-crystal vacuum monochromator at SSRL. This work complements a large body of literature on the 4d thresholds of these materials. The principal difference is the excitation

$$4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$$

decays via an intra-shell super-Coster-Kronig interaction

$$4d^9 4f^{n+1} \rightarrow 4d^{10} 4f^{n-1} + e^-$$

while the 3d hole decays via a weaker intershell interaction.

This work was supported by NSF-DMR-77-27489 and NSF-DMR-79-13102.

(18) The Measurement of Optical Constants Using Transmission Gratings and Transmission Grating Research

Graduate Student: R. Tatchyn

Faculty: I. Lindau

The first experiment to measure optical constants of gold using transmission gratings has been designed at Stanford over the period

1979-1980 and executed at SSRL during February 1981, on the 4^o branch-line of beam line III. The experiments on the gold gratings were performed in collaboration with several other scientists who contributed on several important points. Principally, these were E. Kallne (Harvard-Smithsonian), J. Kallne (University of Virginia), R. Bartlett (Los Alamos, LASL), J. Dijkstra (Utrecht, Holland), M. Hecht (Stanford), and R. Z. Bachrach (Xerox, PARC). The data from the experiment is currently being processed and analyzed.

In addition to the above experiment, work has also continued on the analysis and investigation of grating properties and characteristics. In addition to our initial publications on gratings,²⁻⁵ we have published additional papers on thermal loading in gratings irradiated with synchrotron light⁵ and on photoemissive effects of synchrotron light on grating structures.⁷ From the practical side, an experiment is being planned by us to measure the thermal loading properties of real gratings at SSRL.

Finally, all the above work is being extended by us to the problem of designing new instrumentation and monochromators for use in the soft x-ray range.²

This work was partially supported by NSF-DMR-77-27489.

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(19) Theoretical Study of the Effects of Electronic Relaxations in Resonant Photoemission Spectra

Graduate Student: S.-J. Oh

Faculty: I. Lindau

(Professor Seb Doniach is strongly associated with this work)

We have extended the theoretical study of the effects of electronic relaxations in resonant photoemission spectra on systems with an incomplete d or f shell such as transition and rare-earth metals (CMR Report 1979-80, P353) by including a finite plasmon lifetime in the discrete plasmon type relaxation. In this case, in addition to the usual plasmon satellite peak with fixed binding energy, we predict the appearance of a new feature, a "fluorescent electron emission" peak, at fixed kinetic energy in the electron energy distribution curves (EDCs). This "fluorescent electron emission" peak is due to the decay channel where the virtually excited intermediate state relaxes to the energy shell so that the final photoemission step simply carries a photoelectron energy characteristic of the intermediate state (a "fluorescent decay"), in close analogy with the usual photon fluorescence in a resonant Raman spectroscopy. This can be thought of as a type of Auger decay involving the excited bound electron.

In order to obtain more specific estimates of the relative strength of the various decay modes involved, we use a very simplified model of a discrete plasmon-type relaxation in which the plasmons are given a finite lifetime. We find that:

1. The "fluorescent emission" peak shows a resonance at photon energy $\hbar\omega = E_M - E_I + \hbar\omega_p$, where E_M and E_I are the energies of the intermediate and initial states, respectively, and $\hbar\omega_p$ is the plasmon energy.

The fluorescent decay channel competes with the usual plasmon decay channel, so that when the lifetime of the

intermediate state is longer than that of the plasmon, the fluorescent decay channel is favored, resulting in a stronger fluorescent emission peak, whereas in the opposite case of longer plasmon lifetime, we have a stronger plasmon stellite peak.

In addition to the rare-earth metal case mentioned above, we expect similar resonant photoemission phenomena for a system of adsorbed atoms or molecules on metal substrates, which has been confirmed experimentally.¹ We feel that this system is more likely to show the fluorescent electron emission effect, and the quantitative study of this peak and its comparison with the plasmon satellite structure could lead to a direct experimental handle on the lifetimes of the intermediate state and the plasmon, and hence on the physics of relaxation in excited atomic/molecular states.

This work was partially supported by NSF-DMR-79-13102.

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(20) Resonant Photoemission Studies of Mixed-Valence, Reduced-Moment, and Antiferromagnetic Cerium Compounds

Graduate Student: S.-J. Oh

Professional Associate: J. W. Allen (Xerox Palo Alto Research Center)

Faculty: I. Lindau

We have made resonant photoemission measurements to determine the position and width of the Ce $4f^1$ state in several Ce compounds with different magnetic properties. The materials studied were CeBi, which is an ordinary antiferromagnet with a moment appropriate to a Ce³⁺ ion, CeAl₂ and CeIn₃, which both show magnetic moments reduced from that of a Ce³⁺ ion, and CePd₃, which is of mixed valence and shows a loss of magnetic moment upon cooling. The determination of the position E_f and width δ of the Ce $4f^1$ state in these compounds using photoemission is especially important in understanding the interplay of charge and spin fluctuations, i.e., the relation between the electron charge measurement

of photoemission experiments and the electron spin measurement of neutron scattering experiments.

In this work, the identification of the $4f^1$ state utilizes the large resonant enhancement of $4f$ photoemission for photon energy just above the $4d$ photoabsorption threshold, as reported and discussed for γ -Ce before.² As previously found for γ -Ce, both the binding energies E_f and the widths Δ of $4f$ levels in all the integral-valence materials studied are much larger than commonly expected. Historically, E_f was estimated to be ~ 0.1 eV and Δ to be ~ 10 meV. However, in this work, we have determined E_f to be $2.1 \sim 3.2$ eV (3.2, 2.8, 2.1, and 2.2 eV for CeBi, CeAl₂, CeIn₃ and γ -Ce, respectively), and Δ to be $0.3 \sim 0.8$ eV (0.3, 0.65, 0.5, and 0.8 eV for CeBi, CeAl₂, CeIn₃ and γ -Ce, respectively). Our measurements, however, are consistent with the commonly used model of the Virtual-Bound-State (VBS), local moment, Kondo-type spin fluctuation model for the interplay of charge and spin fluctuations. In this model, the $4f^1$ state is regarded as a virtual bound state supporting a local moment with Kondo-type spin fluctuations, and the Schrieffer-Wolff transformation is used to express the Kondo temperature T_k in terms of E_f and Δ by the relation

$$kT_k \propto \exp(-\pi E_f/2\Delta)$$

Although the measured E_f and Δ are both much larger than previously believed, E_f/Δ gives the same order of magnitude as before, which is consistent with virtual-bound-state models. The $4f$ emission lineshapes extracted from our data can be well fit by the Lorentzian lineshapes convolved with a Gaussian experimental resolution function, which also qualitatively supports the VBS model for the integral-valence materials.

For mixed-valence CePd₃, the $4f$ emission impinges on the Fermi level, in agreement with XPS data and measurements on other mixed-valence compounds. The $4f$ emission is not well fit by a Lorentzian, and its shape is more typical of a band density of states, suggesting extensive $5d$ - $4f$ hybridization.

Reference Publications:

1. J. W. Allen, S.-J. Oh, I. Lindau, J. M. Lawrence, L. I. Johansson, and S. B. Hagström, Phys. Rev. Lett. 46, 1100

(1981), and the Proceedings of the International Conference of Fluctuating Valence Solid, Santa Barbara, California, January 1981.

2. L. I. Johansson, J. W. Allen, T. Gustafsson, I. Lindau, and S. B. M. Hagström, Solid State Commun. 28, 53 (1978).

(21) Theoretical Study of the Effects of Screening in the Core-Level XPS of the Mixed-Valence System

Graduate Student: S.-J. Oh

Faculty: I. Lindau

(Professor Seb Doniach is strongly associated with this work)

The x-ray core-level photoelectron spectroscopy (XPS) on the mixed-valence compounds show two groups of multiplets corresponding to the $4f^n$ and the $4f^{n+1}$ configurations, respectively. The ratio of the areas under the two multiplet structures was sometimes assumed to give the valence in the ground state. This assumption, however, neglects the effect of the electron screening in the final state of the photoemission measurement, and may be quite misleading since the core-hole created in XPS can pull down the unoccupied localized level ($4f$ state in this case) below the Fermi level, and a conduction electron near the Fermi level may drop into this level to screen the core-hole. In fact, Schönhammer and Gunnarsson showed that for a system with a strong hybridization between conduction electrons and the localized electron state, most of the spectral weight goes to this "fully screened" peak, whereas for the weak coupling case the "unscreened" peak is dominant.¹

We have studied this effect of the electron screening in the XPS spectra of the mixed-valence system using Anderson's model Hamiltonian and the Green's function decoupling scheme used by Hewson.² Since the photoemission cross section is proportional to the imaginary part of the core-hole Green's function, we calculated the hole Green's function by decoupling conduction electrons from the localized $4f$ electrons. We found that for the case of a weak coupling between conduction electrons and $4f$ electrons, the ratio of the areas under the two peaks corresponding to the $4f^n$ and the $4f^{n+1}$ configurations closely corresponds to the initial state valence, but as we increase the hybridization strength, more weight is transferred to the $4f^{n+1}$ peak and another peak corresponding to the

$4f^{n+2}$ configuration appears. We interpret this as an effect of the final state screening where a conduction electron near the Fermi level drops down to the unoccupied $4f$ level pulled below the Fermi level by the core-hole, thus making fully screened states of the $4f^{n+1}$ (from the $4f^n$ initial component), and the $4f^{n+2}$ (from the $4f^{n+1}$ initial component) configurations.

Reference Publications:

1. K. Schönhammer and O. Gunnarsson, Solid State Commun. 23, 691 (1977), and 26, 147, 399 (1978).
2. A. C. Hewson, Phys. Rev. 144, 420 (1966), and A. C. Hewson and M. J. Zuckermann, Phys. Lett. 20, 219 (1966).

(22) Resonant Photoemission of 3d States and the Valence Band Satellites in Nickel Compounds

Graduate Student: S.-J. Oh

Professional Associate: J. W. Allen (Xerox Palo Alto Research Center)

Faculty: I. Lindau

The aim of this work is to determine the photon energy dependence of valence band photoemission from various nickel compounds for photon energies in the vicinity of the nickel 3p binding energy, and shed some light on the interpretation of the Ni metal valence band photoemission including the "6eV" satellite. We have obtained photoemission data for NiO and NiTe, and studied the resonance behavior of Cu and Cu₂O near Cu 3p edge.

NiO is a Mott insulator having the Ni^{2+} ($3d^8$) configuration where the Ni 3d electrons are localized. NiTe is a paramagnetic metal with $Ni\ 3d^n$ configuration where n is between 9 and 10. The valence band photoemission spectra for both of these Ni compounds show satellite structures about 6 ~ 7 eV below the main Ni 3d emission, analogous to the Ni metal valence band photoemission. Constant-Initial State-Spectra (CIS's) were taken to measure the variations of the intensity of these satellites and main 3d bands as a function of the photon energy near the Ni 3p edge. For both compounds, the CIS for the satellite shows a strong Fano type resonance, and that for the main 3d band emissions has a characteristic interference dip. These resonance behaviors are just like those of the Ni metal "6eV" satellite and main 3d emissions.

We interpret these resonance behaviors as an atomic effect, since they appear in various Ni compounds having either localized or delocalized Ni 3d electrons. The CIS's can be fit by Fano lineshapes arising from the interference between a discrete state ($3p^5 3d^{n+1}$) and continuum states ($3p^6 3d^{n-1} ql$). This interpretation, which requires 3d holes in the initial state, is supported by the data on Cu and Cu_2O , which have $3d^{10}$ configuration. The valence band photoemission spectra of Cu and Cu_2O both have satellites about 12 eV below the Fermi level, and they show resonant enhancements at the Cu 3p edge. However, we observed that (i) the resonance of the satellite is much smaller than Ni metal and NiO, and (ii) the main 3d band shows no appreciable resonance. This is expected from the above interpretation, since Cu and Cu_2O have filled 3d bands and cannot be excited to the discrete state ($3p^5 3d^{n+1}$) by photons.

From the strong interference in the main 3d emission of Ni metal, we believe therefore that the Ni main band has contributions from a $3d^n$ final state, and accordingly that the "6eV" satellite comes from a $3d^n$ final state, in contrast to the earlier view.²

Reference Publications:

1. Se-Jung Oh, I. Lindau, J. W. Allen, and J. C. Mikkelsen, Bull. Am. Phys. Soc. 26, No. 3 (1981).
2. G. Guillot, et al., Phys. Rev. Lett. 32, 1632 (1977).

59. SOLID STATE CHEMISTRY

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Agency Support:

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NSF-MRL through CMR - Thrust Program on Noncrystalline Metals
ARACOR
EPRI-RP-979-10

(1) Solid Oxide Electrolytes and Related Electrochemical Cells

Objective:

To utilize solid oxide electrolytes to study thermodynamic and kinetic properties of metal-oxygen systems. To study the electrolytic properties of zirconia electrolytes, with particular reference to property and microstructural changes that accompany high temperature annealing, typical of service conditions.

Approach:

The ac conductivity of representative commercially available zirconia - yttria electrolytes - $\text{ZrO}_2 + X \text{ mole } \% \text{ Y}_2\text{O}_3$, with $X=0.045, 0.07, 0.08$ and 0.10 - with porous Pt electrodes is measured over a temperature range of $400 - 1000^\circ\text{C}$ and a frequency range of 2HZ to

400 KHZ. The total conductivity is separated into the bulk conductivity, grain boundary conductivity, and electrode polarization by analysis of complex impedance plots. Particular emphasis is placed on changes in these properties upon annealing (aging) and relating these changes to concurrent microstructural changes, as evidenced by optical, scanning electron microscopy (SEM), transmission electron microscopy (TEM), microchemical analysis, and X-ray diffraction.

Research report:

Several significant observations have been made in the past year on partially stabilized zirconia (PSZ) and fully stabilized zirconia (FSZ).

- There is a substantial decrease in conductivity (σ) in PSZ upon annealing at temperatures of 800°, 900°, and 1000°C.
- The above decrease in σ is related to the following observed microstructural changes:
 - segregation of an yttria-rich layer at the grain boundaries and triple points
 - precipitation of tetragonal ZrO_2 from the cubic phase
 - formation of ordered microdomains of $\text{Zr}_3\text{Y}_4\text{O}_2$ within the disordered cubic phase
- Slower aging rates were found in PSZ with larger grain size, whereas the opposite trend was observed for FSZ.
- Aging of fully stabilized zirconia using scandia (Sc_2O_3) was much faster than the yttria stabilized zirconia, because of an increased ordering tendency.
- Annealing PSZ in an SO_2 ambient caused an increase in σ by the generation of the free electrons

Explanation of these phenomena, along with a consideration of the practical implications, has been accomplished.

(2) Analysis of Dynamic Reacting Systems Using Mass Spectrometric Techniques; Control of Impurities in the Epitaxial Growth of Gallium Arsenide

Objective:

To analyze crystal growth vapor ambients, especially those for GaAs, in order to gain information on impurities introduced from the vapor during crystal growth. To modify the growth processes, in light of the above information, in order to decrease contamination.

Approach:

A molecular beam sampling technique has been developed in order to reliably transfer gas samples from a high temperature (up to 900°C) atmospheric pressure ambient to a mass analyzer. This is achieved by rapid expansion of a gas sample into a three stage differentially pumped system. A series of orifices, slits on mechanical chopping delivers a modulated molecular beam to a quadrupole mass analyzer with subsequent phase lock detection.

As a result of studies of molecular beam mass spectrometry (MBMS), we are pursuing two modifications of liquid phase epitaxial growth (LPE). The first utilizes in situ chemical getters that are intended to rapidly and completely remove oxygen for the liquid metal solvent. The second approach utilizes a zirconia electrolyte tube as container for the liquid metal solvent. With suitable electrodes, one may monitor the oxygen in situ, as well as electrochemically removing it.

Research Report:

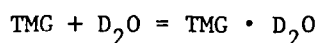
A. Molecular Beam Mass Spectrometry

The recent MBMS activity has emphasized two major topics: improved beam alignment and improved calibration using a calibrated gas internal standard; and the study of the interaction of metalorganics (MO) with oxygen containing species.

Techniques have been developed, using a calibrated gas mixture, that improve the following aspects of the MBMS method: beam alignment; calibration of the entire system response; and interpretation of specific peak heights by use of the xenon internal standard.

The fragmentation patterns of trimethyl gallium (TMG) has been determined prior to a study of the chemical interaction of TMG with

oxygen containing species in the temperature range of room temperature to 500°C. No reaction is observed between O₂ and TMG; however, substantial concentration of a complex - TMG • D₂O - are observed. (D₂O was used instead of H₂O to avoid background problems.) An equilibrium constant for the reaction



has been estimated as 8×10^{-4} at room temperature. The complex appears to be stable up to ~330°C. The implications of these results on OM chemical vapor deposition is being studied.

B. Deoxygenation of Gallium Solvent for Liquid Phase Epitaxial Deposition of GaAs.

I. In situ Chemical Deoxygenation

Small amounts of the elements Ti and Zr are directly added to liquid Ga prior to LPE growth. There is a significant change in properties with these additions: generally p-type layers are obtained, with consistently high mobilities for p-type GaAs (350-460 cm²(volt sec.)). Recent study has emphasized the following: the kinetics of deoxygenation, using this technique; the interplay between concurrent hydrogen annealing and in situ gettering; and the effectiveness of other reactive metals.

II. Electrochemical Deoxygenation

A vertical LPE growth technique using a partially stabilized ZrO₂•Y₂O₃ (PSZ) tube as container for the Ga solvent is being developed. The techniques for crystal growth and for electrochemical monitoring of the oxygen activity have been developed and a study of the layer properties as a function of the oxygen activity in the melt is currently underway.

(3) Corrosion of Heat Exchanger Tubes in Fluidized Bed Coal Combustion

Objective:

To simulate, in a small laboratory scale apparatus, the oxygen and sulfur potentials representative of a full scale fluidized bed coal reactor. To evaluate specific alloys in the above system and characterize the sulfidation-oxidation corrosion morphology and mechanism.

Approach:

Various carbon-sulfur potentials are developed using differing CO/CO₂ gas ratios which are passed over CaSO_{4(s)} or CaS_(s) at different temperatures. The resulting gas is then introduced into a furnace which contains samples of the alloys in question. After a given time at temperature, the samples are quenched and examined by various metallographic and X-ray techniques to characterize the corrosion products.

Research Report:

It has been established that corrosion morphologies similar to those encountered in a full scale fluidized bed coal combustion can be achieved in a laboratory scale apparatus. An approximate transition point, expressed in terms of oxygen and sulfur chemical potential, is obtained for pure oxidation and combined oxidation-sulfidation. This transition is significant since the latter mechanism leads to more severe corrosion.

(4) Solubility and Diffusivity of Chromium in Gallium Arsenide

Objective:

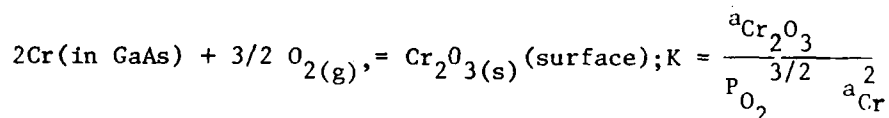
To establish the chemical diffusion coefficient of chromium (Cr) in gallium arsenide (GaAs) for well defined diffusion sources and sinks. To relate the diffusion behavior and electrical activity of Cr in GaAs to detect models for Cr in GaAs.

Approach:

To establish well defined diffusion sources and sinks for Cr diffusion, the phase relations for appropriate isothermal section of the Ga-As-Cr system is determined. Composition in ternary tie triangles correspond to univariant points, thus, specifying temperature in these regions fixes the chemical potentials of the three components. Solubility and chemical diffusion is studied using such compositions for a Cr source or sink.

Research Report:

Major activity has been devoted to verifying and extending information on the three binaries involving Ga-As-Cr and deducing, from this information, the possible isothermal sections for the ternary system in the temperature range of 600-1000°C. Preliminary to diffusion studies, we have studied the surface degradation of GaAs wafers in closed ampoules as a function of temperature and ambient atmosphere. Serious surface degradation occurs above 900°C, even in the presence of excess As. Preliminary in-diffusion and out-diffusion profiles have been measured using closed quartz ampoules. Particularly significant is the control of the oxygen chemical potential in the ampoule using metal-metal oxide couples to define the oxygen potential; the formation of Cr_2O_3 at the surface, according to the reaction below, relates the surface chromium activity to the oxygen potential.



Using this well defined diffusion sink, our results differ significantly from those reported by previous investigators.

Reference Publications:

1. H. Dun and D. A. Stevenson, "Observations on Binary Clusters Formed Upon Expansion of Argon Mixtures," *Chemical Physics* 52, 469-479, (1980).
2. D. A. Stevenson, P. I. Ketruch, S. C. Chang, and A. Borshchevsky, "The Influence of Ti and Zr Additions on GaAs Liquid Phase Epitaxial Growth," *Applied Physics Letters*, 37, (9), 832-834 (1980).
3. T. W. Barbee, Jr., R. G. Walmsley, A. F. Marshall, D. L. Keith and D. A. Stevenson, "Phase Separation in Vapor Quench Synthesized Noncrystalline Copper-Zirconium Alloys," *Applied Physics Letters* 38, (3) p. 132 (1981).
4. B. Heshmatpour and D. A. Stevenson, "Experimental Problems in the Use of Solid Oxide Electrolytes," accepted for Publication; *J. Applied Electrochem.*
5. D. W. Kisker and D. A. Stevenson, "Molecular Beam Mass Spectrometry Studies of Vapor Phase Reactions of Organometallic Compounds," accepted for publication *Proceedings of the Eighth International Conference on Chemical Vapor Deposition.*
6. F. K. Moghadam, T. Yamashita and D. A. Stevenson, "Characterization of Yttria-Stabilized Zirconia Oxygen Solid Electrolytes," accepted for publication, *Advances in Ceramics.*
7. B. Heshmatpour and D. A. Stevenson, "The Influence of Solute Additions of Copper and Silver on the Diffusivity and Thermodynamic Properties of Oxygen in Liquid Indium," submitted for publication.
8. F. K. Moghadam and D. A. Stevenson, "Influence of Annealing on the Electrical Conductivity of Polycrystalline $\text{ZrO}_2 + 8 \text{ wt } \% \text{Y}_2\text{O}_3$," submitted for publication.

60. THERMOPHOTOVOLTAIC SOLAR ENERGY CONVERSION

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*Received Ph.D. during
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Agency Support:

EPRI 790-2

Technical Objectives:

A thermophotovoltaic (TPV) converter is a direct conversion heat engine that converts incandescent radiation from a hot surface (2000°C) into electricity by means of a photovoltaic cell. The objective of this program is to obtain a realistic appraisal of the achievable energy conversion efficiency using silicon photovoltaic cells in a thermophotovoltaic energy converter. Efficiencies over 35 percent are hoped for. These high efficiencies are achieved by recycling the portion of the spectrum that the TPV cell cannot use (mostly at wavelengths greater than 1 μ m) back to the radiator.

Approach:

Based on results of numerical simulations of TPV conversion a preliminary TPV cell was designed. Because of the unique requirements in TPV conversion this cell differs considerably from a typical solar cell. Current efforts involve bringing the cell fabrication to a sufficient level of sophistication to determine if there exist any reason why the expected high efficiencies cannot be achieved. The program

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strategy is to: (a) fabricate TPV cells, (b) measure their efficiency and other relevant parameters, (c) compare the results with the TPV modeling program to characterize the physical processes operative in the cells (our TPV cells operate with a broad spectrum incandescent radiant flux of 300 W/cm^2 , an intensity sufficient to produce effects not observed in normal silicon solar cells), (d) adjust the TPV model with new parameters as necessary, (e) redesign the cell fabrication to improve performance, and (f) iterate through the above steps.

Research Report:

Nineteen runs of TPV cells have been completed. Their energy conversion efficiency has improved from 6 percent in the first cell to a current 29 percent. All of the important parameters have been characterized. Current cells are limited by four mechanisms: (1) base region carrier recombination, (2) contact area surface recombination, (3) contact area infrared absorptance, and (4) scattering of infrared radiator to beyond the critical angle for escape by the top contact grid. Programs addressing each of these areas are underway. Preliminary results in reducing these loss mechanisms have been encouraging. While these results have not been incorporated into complete TPV cells, the TPV model predicts an efficiency of 35 percent when using these values. Presently we estimate that highly developed TPV cells could achieve efficiencies between 40 and 45 percent.

Publications:

J. A. Borsuk and R. M. Swanson, "Current Transient Spectroscopy: A High Sensitivity DLTS System", IEEE Transactions on Electron Devices, Vol. ED-27, No. 12 (December 1980).

61. OHMIC HETEROJUNCTION CONTACTS WITH LOW INTERFACIAL RECOMBINATION
VELOCITY

R. M. Swanson, Assistant Professor, Electrical Engineering

Technical Staff:

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Graduate Student:

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Agency Support:

JSEP DAAG 29-79-C-0047

Technical Objective:

The objective of this ongoing project is to produce ohmic semiconductor contacts to emitters which have low minority-carrier recombination velocity in which to improve emitter efficiency.

Research Report:

Optical studies of the films deposited using the small RF heated AP Hugle CVD reactor confirmed the anticipated dependence of absorption coefficient and refractive index on oxygen content. Sheet resistance measurements of as-deposited and annealed films also indicated that deposition of these SIPOS films was a reproducible process and that control of the nitrous oxide flow rate provided a feasible mechanism for control of the film's optical and electrical properties. The results of the optical studies are to be published in the Journal of the Electrochemical Society under the title "Optical Absorption of Thin SIPOS Films".

Subsequent to the initial feasibility studies, it was deemed beneficial to transfer the deposition process to a hot-wall CVD tube in the ultra-clean room facility. The hot-wall process while suffering from

the drawback of reduced deposition rates has a potential for greater uniformity. The mass flow controllers in this hot-wall CVD tube are controlled by servovalves and promise greater repeatability than the manual needle valves used in the smaller RF unit. Since the hot-wall tube (henceforth referred to as the CVD tube) possessed a four inch diameter, providing a sufficiently high nitrogen carrier flow rate to assure a uniform boundary layer at the wafer surface presented some unanticipated problems. At the high flow rates needed, (100 liters/min), the gas stream has insufficient time to thermally equilibrate. The resulting temperature gradient between susceptor and gas stream resulted in gross nonuniformities in the deposited films. Rectification of this problem required a redesign of the tube to include a preheating mechanism for the large volumetric flow of the carrier gas. An initial investigation proved the feasibility of the preheat concept. Although a first order modeling marginally favored a single channel preheat tube, a twin parallel design was chosen to minimize pressure drops in the preheat system. Further refinements in the tube geometry led to insertion of a flow smoothing baffle and a redesigned susceptor and end cap to minimize wafer defects due to particulate shedding from the tube walls. SIPOS films currently deposited exhibit very good uniformity across a two inch wafer.

Pursuant to the resolution of the uniformity problem, studies were conducted to evaluate the process parameters necessary to achieve an acceptably low sheet resistance in these films. These films, when doped as deposited, display a wide range of resistivities depending upon the annealing conditions. For a typical 1000°C, 30 min. anneal, the resistivities range from .05 to 30 ohm-centimeters for the oxygen concentrations used in the study. An evaluation of various etchants indicate that the $\text{NH}_4\text{F}:\text{HF}$ and $\text{HNO}_3:\text{NH}_4\text{F}$ systems are selective etchants for SiO_2 and SIPOS, respectively. The etching differentials are sufficient to compensate for the tolerances encountered in standard wet etching processes.

With this data available, a mask set has been designed to investigate the efficacy of SIPOS in heterojunction contact structures. The mask set incorporates transistor structures designed to separate the various components of the base defect current thereby allowing direct observation of the effect of the contact structure on reverse injection characteristics. The test structure also includes structures that allow measurements of the Hall effect, thermoelectric power, and field effect conductance modulation. Isojunctions are also incorporated to evaluate contact resistance.

These devices are currently in the fabrication stage. Measurements of the I-V and C-V characteristics of these devices should serve to narrow the focus for the next stage of the investigation.

Publication:

Y. Kwark and R. M. Swanson, "Optical Absorption of Thin SIPOS Films", accepted for publication in the J. Electrochem. Soc.

62. FUNDAMENTAL ASPECTS OF REACTIVITY IN INORGANIC SYSTEMS

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Agency Support:

NIH GM13638-15
NSF CHE79-08633
NSF CHE77-22722

Technical Objective:

A. Electronic Interactions between Metal Ions. One manifestation of such interactions is net electron transfer in oxidation-reduction reactions. Of interest are the rates as function of the properties of the ligands associated with the metal ions as well as of the matter separating them. The principles governing the processes are important as providing a basic understanding of one of the major classes of chemical change, but they also have some relevance to understanding electronic conduction on a molecular level. The electronic interactions manifest themselves also in some special properties possessed by mixed-valence molecules. Such species often show a near infra red absorption

which arises from metal-to-metal electron transfer, and provides a measure of the electronic coupling between the metal centers.

B. Basic Chemistry of Heavy Transition Elements. The special efficacy of some of the heavy transition metals as catalysts is well known, as is the fact that their chemistry can differ markedly from that of their congeners in the first transition period. A systematic exploration of the chemistry of selected members is in progress, with the goal of understanding their reactivity in basic terms.

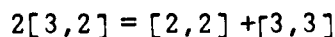
C. A research program, involving collaboration between industry, a group at Cal Tech (Anson) and three groups at Stanford (Boudart, Collman and Taube) is in progress with the goal of developing a catalyst for the oxygen cathode. The general approach is to synthesize metal-containing species which make possible multicolor, and it is hoped, multivalent attack on O_2 by the reduced metal complex. The catalysts are to be adsorbed or otherwise attached to the electrode surface, so that the oxidized form resulting from the reaction of the reduced form with O_2 can readily absorb electrons from the electrode, completing the catalytic cycle.

Research Report:

A. Electronic Interactions between Metal Ions. In continued work on mixed valence molecules, we have attempted to assess the contribution to the stability of a species such as



resulting from electron delocalization between the metal centers. An upper limit on this is set by ΔG° for the comproportionation reaction



which in the case of I amounts to -500 cal per mole. About half of this is purely electrostatic in origin, charge repulsion in the isovalent state being greater than in the mixed valence, so that in an upper limit to stabilization resulting from delocalization is 250 cal. An approximate estimate can be made from the oscillator strength of the inter-valence band and the result gotten in this way is 50 cal per mole. Two additional factors need to be allowed for: (i) the enhancement in the stability of the [3,2] arising from the fact that back-bonding from Ru(II) to the bridging ligand increases when a positive charge is placed on the ligand, (ii) instability in the [2,2] arising from electron repulsion—both metals put electron density into the same orbital of the bridging ligand. Efforts are being made to quantify these two factors.

B. New methods for preparing osmium complexes are being tested and show considerable promise. A point of special interest is the enormous tendency for back-bonding in complexes of the type $\text{Os}^{\text{II}}(\text{NH}_3)_5\text{L}$ where L is a π acid ligand. The exploration of this promising subject has been hampered by the lack of convenient preparative methods.

Reference Publications:

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2. John D. Buhr and Henry Taube, "Dinitrogen Complexes of Osmium(III) Haloammines," *Inorg. Chem.* 1980, 19, 2425.
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4. Yann Hung, Wei-Jen Kung and Henry Taube, "Aquo Chemistry of Monoarene Complexes of Osmium(II) and Ruthenium(II)," *Inorg. Chem.*, 1981, 20, 457.
5. C. A. Stein and Henry Taube, "Manifestations of Sulfur to Sulfur Through-Bond Interactions in Complex Ion Spectra," *J. Amer. Chem. Soc.*, 1981, 103, 693.

63. SEMICONDUCTOR PROCESSING, GAS DISCHARGES, GROWTH-DISSOLUTION AND SURFACE BEHAVIOR OF CRYSTALS, BIOMATERIALS

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**Received M.S. during report period

Agency Support:

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NASA NAS8-33110
LLL 269-5501
NASA/Ames NCC-2-125
NSF-MRL through CMR

Technical Objectives:

(a) To gain an atomistic level of understanding that is quantitatively predictive concerning the key features of semiconductor processing; i.e., oxidation, film formation, diffusion, etc. To fully control and exploit these processes in integrated circuit technology using both a macroscopic and a microscopic level of understanding and a representation that is both atomistic and parametric.

(b) To understand the fundamental principles of gas discharges so that they may be utilized in various applications such as sputtering, environmental control, surface doping and information displays.

(c) To gain a complete and quantitative understanding of the crystallization process from any media. To investigate the various

contributions which comprise the energy of either a stationary or a moving interface plus how this energy changes with the detailed topography and state variables (C, T, P, ϕ) of the interface.

(d) to develop devices and techniques for non-invasively monitoring living systems. To investigate membrane properties and the growth of essential body materials; e.g., nerves.

Approach:

(a) Theoretical investigation of all the processes involved in the thermal oxidation of silicon, the reactive sputtering of silicon and beam deposition of films. Experimental studies on the enhancement of the oxidation velocity via corona charging and via U.V. radiation, on phosphorus redistribution during oxidation, on the reactive sputtering of SiO_x ($0 < x < 2$) and other MO_x compounds, on the multiple source deposition of SiC and on the deposition of layered materials.

(b) Experimental and theoretical investigation of plasma bubbles developed during gas discharges with application to A.C. plasma display panels.

(c) Theoretical and experimental investigation of crystal growth and interface instability in the compound CsCdCl_3 . Theoretical investigation of the dissolution of quartz and various silicates.

(d) Theoretical and experimental development of techniques for monitoring various components of the electrical equivalent circuit of human skin (in vivo). Experimental investigation of the regrowth of nerves in rats (in vivo).

Research Report:

(a) 1. A study of reactive sputter deposition of SiO_x films ($0 < x < 2$) onto room temperature (100) single crystal silicon substrates has been performed. In this process, an RF excited, elemental silicon source was used. This source was isolated from the oxygen, which was introduced into the vacuum system at the substrate. The composition of the deposit was determined by the ratio of the incident rates of silicon and oxygen. It has been found that SiO_x films can be deposited at rates

of 3 to 10 Å/sec. The films have been characterized by (1) refractive index, (2) film thickness, (3) electron microprobe analysis, (4) transmission electron microscopy, (5) electrical resistance, and (6) MOS capacitance measurements. The refractive index is observed to vary systematically with oxygen pressure during synthesis and to be dependent upon the incident rate ratio of oxygen to silicon.

2. The synthesis of silicon carbide using two-source and single-source magnetron deposition technology has been investigated. The formation of SiC_x ($0.2 < x < 4$) alloy films has been performed using two-source techniques at substrate temperatures ranging from room temperature to 800°C. Composition, thickness, refractive index, and structure of these films have been determined using electron microprobe, alpha-step stylus, ellipsometry, and x-ray analytical techniques. At the carbon-rich end, the depositions were specular (mirror-like) and light gold or light brown in color. Depositions in the SiC region exhibited many closely spaced colored interference fringes. In the silicon-rich deposits, the surface exhibited a hazy appearance resulting from columnar growth of the silicon. The refractive index of the films was measured and, in the region of stoichiometry, was found to be 2.6 in agreement with the literature value for SiC. X-ray analysis showed a preferred texture to the film revealing the (111) of β -SiC to be parallel to the film surface. The optically determined bandgap for films deposited on sapphire showed it to be about 3.0 eV, which is the bandgap expected for β -SiC.

3. Some present models of the thermal oxidation of Si involve interstitial Si as well as interstitial O species. Reaction between these species leads to interstitial swelling stresses, network structure breaking and silica ring rearrangements. Similar processes may be involved in the formation of SiO_x films by reactive sputtering. For this and other reasons, a need exists to understand in greater detail why silica tetrahedra adopt the configurations they do and how these configurations are altered by interstitial species. We have analyzed the crystalline polymorphs of SiO_2 , all of which are made from relatively non-deformable oxygen tetrahedra containing interstitial silicons with

a pair of adjacent tetrahedra sharing a corner. These polymorphs can be described in terms of a dimer of two tetrahedra as the symmetry unit, rather than the conventional 6-membered ring unit, with all configurations depending on only two geometrical variables: (1) the Si-O-Si bridging angle and (2) the pair of dihedral angles made by a face of each tetrahedron relative to a fixed reference frame. For all the known SiO_2 crystalline structures, these two variables exhibit remarkably simple values relative to the full range of possible variations. It is the closure constraint of the 6-membered rings that appears to be responsible for such a simplification. We have modeled 4, 5 and 6-membered rings and determined the ranges of acceptable ring parameters as well as the orientation of the tetrahedra whose edges form the sides of the ring. We have also developed methods to locate the channels or sites of interstitials in the rings. The extension of this approach to the study of vitreous SiO_2 is under way.

4. The thermal oxidation of silicon, electric field enhanced oxidation of silicon and U.V. enhanced oxidation of silicon, all involve the transport of various oxygen and/or water interstitial species through vitreous SiO_2 . To fully understand these processes and to have them work controllably at lower temperatures, it is necessary to obtain the activation energies for solution and diffusion of interstitial species in SiO_2 . We have used a molecular orbital approach (CNDO/2) to model the interactions of both charged and uncharged O and H-bearing species with the SiO_2 network. Calculations are presently being performed on two clusters: (1) a tetrahedral dimer ($\text{H}_6\text{Si}_2\text{O}_7$), where the interstitial species interacts with the bridging oxygen, and (2) a tetrameric ring ($\text{H}_8\text{Si}_4\text{O}_{12}$) with the interstitial internal to the ring. Later calculations will treat the characteristic 6-membered ring ($\text{H}_{12}\text{Si}_6\text{O}_{19}$) present in SiO_2 polymorphs. The minimum total energy for O_2 in the tetrameric ring occurs with the O_2 at ring center with its axis parallel to the ring axis (reaction energy, $\Delta G_f = +7.39$ eV). The optimum position of O is in the ring plane between 0.5 \AA and 0.75 \AA from the center (diameter = 3.47 \AA , $\Delta G_f = -3.04$ eV). These calculations suggest dissociated O_2 is strongly adsorbed by SiO_2 but undissociated O_2 is not.

5. An experimental and analytical research program has been initiated to develop multilayer x-ray dispersion elements for three specific application areas and to develop a better basic understanding of their synthesis process. The three specific application areas are (1) Low Energy Application: Development of multilayer x-ray mirrors for the 100 eV to 1000 eV range with emphasis on systems that would provide five narrow channels ($E/\Delta E \approx 30$) at suggested energies of 100, 270, 440, 670, and 900 eV, for an incidence angle of 25° . (2) Higher Energy Applications on Curved Substrates: Applications here are oriented towards a demonstration project involving an 8 keV Kirkpatrick-Baez x-ray microscope. The latter is a 22X magnification device with an approximately 16.5 meter radius of curvature in each of the successive cylindrical reflectors. Angles of incidence are 2.054° and 1.946° , respectively. These coated microscopes are designed to extend present capabilities beyond the 3-4 keV range. We anticipate a need for other coatings emphasizing heliogenic emission lines of titanium (4.7 keV), chromium (5.7 keV), cobalt (7.2 keV, etc.). (3) Other Research Applications: (a) multilayer coatings on transparent substrates, such as thin ($< 0.5 \mu\text{m}$) polyimide, for use as sub-keV x-ray beam splitters, (b) jelly roll zone plate lenses in which finer outer zones ($\sim 500 \text{ \AA} - 1500 \text{ \AA}$) can be used to form shorter focal length, and perhaps more efficient, zone plate lenses.

The synthesis process research centers on definition of interface character between the individual layers in the multilayer structure. The effects of process parameters, including system pressure, substrate to source spacing, and deposition rate, are being explored. Substrate roughness effects and post synthesis annealing will also be investigated.

(b) 1. Our discovery of electric (plasma) bubble domains has led us to consider their technological potential in computer displays. Our initial work has been directed toward understanding the physical principles underlying domain formation. We now intend to further explore both the underlying physics and the feasibility of constructing a bubble shift register. This bubble shift register would form the basis of a new type of shift-addressed A.C. plasma display. For this purpose we are under-

taking the following investigative plan. Goal 1: To understand the influence of gap length, dielectric thickness, dielectric constant, applied voltage amplitude, waveshape, and frequency on plasma domain characteristics. To measure the functional dependence of the domain radius. Goal 2: To develop a first-order theory of the functional dependence of the domain radius on gap length, dielectric thickness, dielectric constant, maximum and minimum sustain voltage, and applied voltage amplitude. Goal 3: To demonstrate controlled generation and annihilation of isolated plasma bubbles and assess the feasibility of propagating plasma bubbles using either field access or conductor access. Goal 4: To fabricate an experimental single-line plasma bubble shift register for evaluation.

(c) 1. A study has been made of interface field effects on interface instability during crystal growth. From the calculated interface field-influenced solute profiles in the liquid and solid, the change in the "Constitutional Supercooling Criterion (CSC)" in the liquid has been calculated. This is shown to be a very significant effect in some cases. An interface instability analysis has been made for a planar interface growing in the constrained growth mode using isotropic interface free energy, γ , and infinitely rapid interface attachment kinetics. Results for the perturbation amplitude response, δ/ϵ , as a function of wavelength, λ , for this linear system have been calculated for various types of interface fields and compared with the Mullins and Sekerka results. Significant differences are found for reasonable interface field strengths. In the experimental portion of this work, a major study has been made on the system CsCdCl_3 as host and CsCoCl_3 as a solute. Czochralski grown crystals at fixed rotation rate with varying V , plus at fixed V with varying rotation rate, have been prepared and the CsCoCl_3 distribution determined. These distributions agree reasonably well with the theoretical predictions and yield values for the interface field interaction parameter in the solid; i.e., a β_S value of (a) 0.1745 kT for the $\langle 0001 \rangle$ orientation and (b) 0.0720 kT for the $\langle 10\bar{1}0 \rangle$ orientation with a liquid solute content of 1% CsCoCl_3 , provided we set $\beta_L = 0$ in both cases. In an attempt to obtain all the material parameters for this

system needed to test the interface instability analysis, the following have also been measured: (i) phase diagram distribution coefficient, k_0 , at small solute contents, (ii) liquidus slope, m_L , at small solute contents, (iii) latent heat of fusion, (iv) heat capacity of the liquid and solid, (v) density of liquid and solid, plus (vi) viscosity of the liquid. However, our goal has been thwarted because of the inability to meaningfully measure the thermal conductivity of the solid due to its transparency and due to the strong dependence of its transparency upon the doping level of the solid. Thus, no quantitative comparison of interface instability predictions with experimental data has been possible for this system.

2. The sequence of mineral reactions involving zeolite and other authigenic phases in tuffaceous sedimentary rocks has been studied and can be explained by growth and dissolution reaction kinetics. Kinetic factors appear to determine the specific authigenic phases which form and the temporal and spatial constraints on the solution composition during irreversible dissolution and growth reactions in glass-bearing rocks. The glass phase generates a high level of supersaturation with respect to a variety of aluminosilicates in the pore fluid and the sequence of assemblages formed during a series of metastable reactions resembles an Ostwald step sequence.

Metastable reactions occur because formation of less stable phases such as gels, clays, and disordered zeolites may lower the total free energy of the glass-bearing system faster than the growth of the stable assemblage including ordered feldspars, quartz, and micas. Eventually, after a series of steps, the most stable silicate assemblage for the bulk composition, temperature, and pressure may form. However, the formation of intermediate metastable phases can delay the attainment of equilibrium by as much as tens of millions of years.

(d) 1. Over the past decade, there has been a growing interest in the electrical characteristics of acupuncture points and in the development of instrumentation to monitor the meridian's condition for human diagnostics. At present, three significant pieces of equipment are on the market and are being used by medical practitioners. A study has

been made of the role of the electrical behavior of skin upon these device measurements. To understand the A.C. conductance response of the skin, the permselectivity nature of the cell membranes as influenced by the isoelectric point of the membrane and the pH of the cellular fluid had to be considered. An electrical equivalent circuit for the skin was developed which included this effect in a diffusional admittance term. In one of these devices, conductivity increases via carrier multiplication from electrolysis had to be considered. A complete description of the observed results was possible, not only in terms of an electrical equivalent circuit, but in terms of the biochemical and cellular elements that are the physiological correlates of these electrical parameters.

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6. R. Chow and W. A. Tiller, "Deformation-Induced Work Function Changes in Cu Single Crystals, Part II: Theoretical," submitted to J. Appl. Phys. (NSF-MRL support)
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64. SOLID STATE ELECTROCHEMISTRY

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Agency Support:

NSF-MRL through CMR
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DOE LBL 4503110

Technical Objectives:

Development and evaluation of new materials for use in solid state electrochemical systems as electrolytes or electrodes. Use of solid state galvanic cells as sensors and to evaluate thermodynamic and kinetic parameters of gases, liquids, and solids. Development of new experimental techniques for the evaluation of transport parameters of species in solids.

Research Report:

(1) Materials for Use in Anion-Conducting Solid Electrolyte Fuel Cell for the Electrochemical Combustion of Coal

Materials are being explored for use as critical components in a novel type of moderate temperature fuel cell for the electrochemical combustion of coal and related carbonaceous solids. The use of a solid electrolyte is a unique feature of this approach, as well as the presence of a mixed-conducting liquid in the negative electrode compartment. This latter material must meet an unusual set of critical requirements, including high chemical diffusivity and solubility of oxygen, chemical stability at the appropriate oxygen partial pressure, and electronic conductivity.

(2) Materials for Use in Lithium- and Proton-Conducting Battery Systems

Experimental research has been undertaken to synthesize and

evaluate solid electrolytes for potential use in high energy battery systems. Recent work has focussed upon materials that are proton conductors, as well as ternary lithium nitride halides, which combine high values of ionic conductivity with attractive thermodynamic stability against either oxidation or reduction.

(3) Enhanced Ionic Conduction Related to Interfaces in Two-Phase Solid Structures

Work is being started to evaluate the basis for the significant increase in the ionic conductivity found in several solids when dispersed particles of a second phase are present in their microstructures. This phenomenon is being studied by the use of materials with multi-layer synthetic microstructures to enhance observable effects. Variation of the preparation conditions will allow the evaluation of various possible causes of these effects.

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65. DEVELOPMENT OF IMPLANTABLE MULTIELECTRODE ARRAYS FOR AN AUDITORY PROSTHESIS

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and Engineering

Graduate Students:

S. A. Shamma (Received PhD during report period.)
N. E. Cotter

Agency Support: NIH-N01-NS-7-2366

Technical Objective:

To develop multielectrode arrays for an auditory prosthesis for the profoundly deaf which works by direct electrical stimulation of the auditory nerve.

Approach:

The principal thrust of this program is to utilize the techniques of high resolution photolithography to fabricate multielectrode arrays for long term stimulation of the auditory nerve. The materials problems involved are those of electrolysis of the electrode metal, deterioration of the insulation materials under protracted exposure to the biologic environment, and delamination of the thin film structures characteristic of planar technology.

Two types of electrode arrays are required, rigid arrays for direct impaling of the auditory nerve and flexible arrays for insertion into the curved scala tympani chamber of the cochlea. We have achieved electrodes having long-term survival using tantalum conductors on a sapphire substrate for the rigid electrodes and a polyimide-tantalum-polyimide sandwich for the flexible electrode. For the rigid electrode the native oxide of the tantalum provides the primary layer of insulation, followed by overcoats of silicon nitride and Parylene. For the flexible electrode, the polyimide upper and lower layers join to form the insulating protection. Life tests of both kinds of electrodes are now in progress.

Reference Publication:

Gerald A. May, Shihab A. Shamma, and Robert L. White, "A Tantalum-on-Sapphire Microelectrode Array, "IEEE Trans. Elec. Dev. Vol. ED-26, 12 (1979).

66. STATE-TO-STATE REACTION DYNAMICS

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Professional Associate:

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Graduate Students:

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Agency Support:

NSF CHE 78-10019
ONR N00014-78-C-0403

Technical Objective:

To understand elementary bimolecular gas-phase reaction processes and gas-surface interactions by preparing well-defined quantum states of the reactants and determining the subsequent quantum states of the reaction products.

Approach:

We prepare specific quantum states of reagent molecules using a laser. The internal state distribution of products from the resulting reaction is then inferred by laser-induced fluorescence or from visible chemiluminescence.

Research Report:

(1) Laser Fluorescence Studies of Surface Dynamics

Laser-induced fluorescence has been used to determine the distribution of internal molecular quantum states of nitric oxide (NO) molecules scattered from a clean, well-ordered Ag(111) surface at several surface temperatures. A room temperature effusive stream of NO, having a flux of approximately $8 \text{ monolayers sec}^{-1}$, was scattered from a surface

which had been sputtered clean and analyzed with Auger Electron Spectroscopy and Low Energy Electron Diffraction in ultra-high vacuum. The surface-scattered molecules were found to have a Boltzmann distribution of rotational states. The rotational temperatures derived from these distributions were found to be significantly less than the scattering surface temperatures, yielding rotational accommodation coefficients of 0.40, 0.42, and 0.26 at surface temperatures of 475 K, 615 K and 720 K respectively. The rotational accommodation of NO on Ag(111), therefore, is inefficient: a fact that is somewhat surprising in light of the known NO/Ag(111) chemisorption bond energy of 25 kcal mol⁻¹.

We have recently installed and characterized a new pulsed, hypersonic molecular beam source. This collimated beam will be used to determine the effect of incident angle, translational energy and internal energy on the gas-surface scattering dynamics. Current operation with unseeded NO produces a 100 μ s pulse of molecules rotationally cooled to 13 K and having an effective beam density at the crystal of approximately 10⁻⁴ Torr. The UHV scattering chamber remains at 3 x 10⁻¹⁰ during pulsed beam operation.

Our studies will soon be expanded to include As₂ scattering from GaAs($\bar{1}\bar{1}\bar{1}$). This system is of interest from both the scattering dynamics and technological points of view in that a) As₂ scattered from GaAs is translationally some 200 K "colder" than the surface temperature and b) the As₂ scattering behavior may play a role in the technologically important process of Molecular Beam Epitaxial growth of III-V compound semiconductors. A chamber for use in these studies has recently been assembled.

The Reaction of Alkaline Earth Atoms with Vibrationally and Rotationally Excited HF

The effect of internal excitation (vibration and rotation) on reaction dynamics is being investigated on the reaction of alkaline earth atoms with hydrogen halides. The specific reaction chosen for

study is $\text{HF} + \text{Sr} \rightarrow \text{SrF} + \text{H}$. This (endothermic) reaction is given sufficient energy to proceed by optically pumping the HF reagent to $v=1$ and selected J levels. A key aspect of this experiment is the use of a lithium niobate optical parametric oscillator which serves as a continuously tunable (1.5 - 4 microns) source of infrared light. This allows a wider selection of HF($v=1$) rotational states than would be possible with a chemical laser.

Recent developments in the experimental setup include the installation of a new 2-chamber, differentially heated source for the alkaline earth atoms. This new addition allows longer running time with no intermittent blocking of the beam. The detection system has been improved by the construction of a new dye laser with increased power and narrower bandwidth. Preliminary experiments in which the SrF product state distributions (only vibrational band heads are resolved) have been performed. Work is in progress to extend the measurements to all HF P and R lines accessible at room temperature. At the same time, polarizers are being installed in the OPO beam in order to use this polarized light to orient the HF molecules either perpendicular or parallel to the incoming Sr beam to determine the effect of orientation on the dynamics.

SECTION D

PUBLICATIONS

SECTION D

PUBLICATIONS SINCE LAST REPORT

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SECTION E

DOCTORAL DISSERTATIONS

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DOCTORAL DISSERTATIONS

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APPENDICES

APPENDIX - I

I. FACULTY MEMBERS PARTICIPATING IN MATERIALS RESEARCH

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S. G. Boxer	Asst. Professor	Chemistry
J. I. Brauman	Professor	Chemistry
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R. H. Bube	Professor	Materials Science & Engineering, Electrical Engineering
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B. Cabrera	Asst. Professor	Physics
J. P. Collman	Professor	Chemistry
N. S. Dixon	Asst. Professor	Physics
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W. M. Fairbank	Professor	Physics

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S. S. Hanna	Professor	Physics
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C. R. Helms	Adjunct Professor	Electrical Engineering
W. C. Herring	Professor	Applied Physics
A. G. Herrmann	Visiting Assoc. Professor	Applied Mechanics
G. Herrmann	Professor	Mechanical Engineering, Applied Mechanics, Civil Engineering
K. O. Hodgson	Assoc. Professor	Chemistry
B. A. Huberman	Consulting Professor	Applied Physics
*R. A. Huggins	Professor	Materials Science & Engineering
*G. S. Kino	Professor	Electrical Engineering, Applied Physics
C. H. Kruger	Professor	Mechanical Engineering,
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APPENDIX - II

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Y. Ilan	Chemistry
P. Irvine	Chemistry
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I. Yarita	Mechanical Engineering
A. Yeh	Chemistry
J. E. Yie	Chemical Engineering
T. Yoneda	Chemical Engineering
L. T. Zitelli	Ginzton Laboratory

APPENDIX - III

III. GRADUATE STUDENTS PARTICIPATING IN MATERIALS RESEARCH PROGRAMS

APPLIED EARTH SCIENCES

B. J. Bartholomeusz	S. H. Slivinsky	V. S. Tripathi
C.-H. Hua		

APPLIED PHYSICS

L. H. Allen	K. A. Fesler	B. B. Pate
C. E. Barker	D. Foley	G. A. Pavlath
S. J. Bending	J. E. Fouquet	M. A. Perez
K. E. Bennett	S. Froyen	D. W. Pettibone
P. A. Bennett	J. B. Green	M. Riazat
M. A. Berding	E. K. Gustafson	D. Rugar
R. A. Bergh	M. H. Hecht	S. T. Ruggiero
J. E. Bowers	F. Hellman	M.-L. Shek
W. F. Carlsen	M. A. Henesian	C. P. Smith
S. Celaschi	J.-M. Heritier	D. G. Stearns
L. A. Christel	J. A. Hildebrand	R. G. Stearns
K. L. Conway	N. M. Hylton	P. A. Stevens
M. J. F. Digonnet	D. B. Kimhi	J. J. Talvacchio
M. S. Di Iorio	H. A. Kunkel	R. L. Thornton
M. D. Duncan	J. Kwo	T. P. Thorpe
W. D. Eades	R. A. Lacy	J. J. W. Tien
S. R. Early	K. F. Lee	F. P. Trebino
C. Eberspacher	M. C. Leifer	A. J. Viescas
J. A. Edighoffer	A. Lietoila	D. Y.-F. Wang
J. M. Eggleston III	K. F. Ludwig	D. G. Weinstein
M. J. Endemann	R. C. Lye	D. L. Weissman-Wenocur
G. W. Faris	D. J. Mael	P. J. K. Wisoff
P. M. Fauchet	F. G. Muennemann	Y. W. Yau
M. M. Fejer	S. A. Newton	R. C. Youngquist
R. D. Feldman	Y. Park	Y. B. Zambre

CHEMICAL ENGINEERING

N. M. Abbas	Y.-L. Cheng	G. E. Gdowski
M. A. Barteau	A. W. M. Chow	R. Gelles
W. S. Borghard	B. W. Duff	W. L. Holstein
L.-T. Chen	P. D. Fitzgibbon	S. Ichikawa
W.-C. Cheng	M.-A. Gashgari	E. Iglesias

CHEMICAL ENGINEERING (continued)

D. S. Inloes	M. A. McDonald	E. M. Stuve
S. W. Jorgensen	B. C. Nguyen	J. W. Thomas, Jr.
J.-J. Lee	S. T. Oyama	D. M. Thornburg
K. V. Lemley	A. J. Pacey	L. Volpe
S. B. Libicki	J. Sanchez-Arrieta	K. J. Watkins
B. K. Lok	S. N. Semerak	J. C. Wright
V. M. Ma	W. J. Smith	

CHEMISTRY

R. I. Altkorn	F. D. Howard IV	M. J. Pellerite
K. Balakrishnan	R. L. Jackson	S. A. Raybuck
A. T. Barfknecht	J. M. Jasinski	H. G. Rennagel
C. E. Barnes	K. M. Kosydar	D. E. Richardson
J. E. Belmont	G. D. Kubiak	M. G. Roelofs
C. S. Bencosme	A. Kuki	C. M. Rynard
S. E. Bott	F. W. Kutzler	K. E. Salomon
P. J. Brothers	H. W. H. Lee	J. L. Sessler
R. R. Bucks	R. F. Loring	S. C. Shatas
G. S. Cartwright	D. R. Lutz	L. M. Smith
C. E. Chidsey	A. M. Madonik	S. G. Stanton
M. S. Co	K. R. Maier	W. Tumas
S. D. Conradson	W. K. Mainquist	G. S. Wann
P. S. Drzaic	J. Marks	D. C. Ware
M. D. Ediger	E. F. McCord	R. S. Weber
A. Flamberg	R. J. D. Miller	R. M. Weis
P. E. L. Flamberg	R. S. Moog	J. F. Wishart
M. E. Foley	C. R. Moylan	L. K. Woo
P. Frank	K. A. Nelson	K. A. Wright
T. L. Frey	N. H. Oliver	B. E. Zebrowski
D. A. Geselowitz	R. W. Olson	K. M. Zero
C. R. Gochanour	D. A. Outka	G. Zhang
J. E. Hahn	F. G. Patterson	

ELECTRICAL ENGINEERING

A. I. Akinwande	G. B. Bronner	N. E. Cotter
S. Ayter	S. Chen	K. Doganis
R. L. Baer	D. Chin	G. Eggermont
J. A. Borsuk	A. N. Chu	S. J. Eglash
D. G. Boyers	P. D. Corl	A. M. Fauchet

ELECTRICAL ENGINEERING (continued)

P. F. Finman	K. K. Liang	J. A. Silberman
J. R. Fruchterman	K. J. Malloy	P. R. Skeath
C. L. Gaeta	D. Mandelkern	W. V. Sorin
R. B. Gold	M. M. Mandurah	F. E. Stanke
S. H. Goodwin	H. Z. Massoud	P. M. Stefan
M. E. Greiner	S. Matsumoto	L. F. Stokes
M. M. Hackert	S. Minagawa	T. Stultz
B. B. Hadimioglu	D. N. Modlin	C.-Y. Su
A. A. Iranmanesh	F. Mohammadi	B. Swaminathan
K. P. Jackson	B. M. R. Moslehi	R. L. Swent
K. G. Jew	J. C.-Y. Ng	S. E. Swirhun
M. T. Jordan	Y. I. Nissim	M. R. T. Tan
T. J. Kane	S.-Y. Oh	R. O. Tatchyn
W. D. Kimura	W. G. Opyd	M. A. Taubenblatt
B. H. Kolner	S. C. Perino	C. Terwilliger
G. K. G. Krieger	D. K. Peterson	H. C. Tuan
M. R. Kump	K. J. Polasko	D. B. Tuckerman
E. Kutlu	J. W. Rouse	C. C. Williams
Y. H. Kwark	A. R. Selfridge	F. C. Wu
L. K. Lam	S. A. Shamma	S. Yoshizumi
S.-C. Lee	J. C. Sheppard	E. M. Young
Y.-S. Lee		

GEOLOGY

H. D. Boek	M. F. Hochella, Jr.	D. C. Pohl
B. Goldstein	K. D. Keefer	J. E. Shigley
A. Hessenbruch		

GEOPHYSICS

T. D. Jones	J. E. Stein	J. D. Walls
W. F. Murphy	C. A. Tosaya	

MATERIALS SCIENCE AND ENGINEERING

K. S. Ahn	W. B. Avery	J. C. Bravman
T. C. Anthony	R. W. Barton	S. M. Brennan
J. A. Aranovich-Magran	N. L. Baumrind	K. W. Carey
R. F. Aspandiar	R. B. Beyers	M. S. Casey
M. Avalos-Borja	N. Bozorg-Grayeli	J. S.-C. Chang

MATERIALS SCIENCE AND ENGINEERING (continued)

M. D. Deal	M. I. Landstrass	M. P. Scott
S. M. De Jesus III	C. Lee	K. L. Seaward
J. P. Doench	C.-T. Lee	S. L. Shinde
J. C. Earthman	Y.-S. Lee	J. Slater
L. E. Eiselstein	G. C. Lesh	J. D. Smith
A. Fischer-Colbrie	P. W. Lew	B. C. Snyder
C. M. Fortmann	T. C. Lowe	J. J. Stephens, Jr.
K. P. Fuchs	A. J. Mark	G. B. Stephenson
J. F. Garber	K. J. Mark	T. Tanaka
R. A. Gasser	M. L. Mecartney	A. Tasooji
M. H. Grabow	M. J. Mills	E. G. Tolf
J. K. Gregory	W. J. Moberly	A. S. Wakita
L. A. Haslim	F. K. Moghadam	R. G. Walmsley
G. A. Henshall	S. Morita	F.-C. M. Wang
M. K. Hibbs	K. F. M. Nelson	J. C. Wei
D. A. Hughes	J. E. Nielsen	J. G. Werthen
V. Jayaram	K. Nishimura	S. L. Westphal
S.-K. Joo	W. C. Oliver	J. E. Wittig
C. Y. Kao	W. A. Orr	C. R. Wolfe
M. E. Kassner	T. Oyama	C.-C. D. Wong
Y.-S. Kim	F. A. Ponce	M. Y. Wu
D. W. Kisker	J. Poris	T. T. Yamashita
A. R. Kobrin	S. A. Raza	D. Yaney
J. B. Kortright	M. T. Resch	K.-S. Yu
D. W. Kum	D. M. Rickey	J. L. Yuen
S. Laderman	M. Rivier	A.-A. Ziaai-Moayyed
A. Landauer	K. R. Rubin	

MECHANICAL ENGINEERING

(including Division of Applied Mechanics)

I. M. Al-Khattat	Y. S. Garud	R. M. Nelson
P. C. Ariessohn	L. A. Gore	V. Ponnaganti
V. G. Baghdasarians	J. K. Gran	R. D. Schlueter
J. S. Chung	C. W. Jackson	N. Shaikh
K. Chung	K. S. Kim	S. Tipton
M. J. Fisher	R. B. King	T. B. Wertheimer

PHYSICS

M. Bassan
S. Benjamin
L. A. Bloomfield
D. A. Browne
N. W. Carlson

D. J. Jackson
K. M. Jones
P. J. Jupiter
K. E. Kihlstrom
L.-S. Lee

T. P. Orlando
W. G. Petro
J. D. Phillips
K. W. Rigby
K. E. Robinson

W. L. Carter
A. L. De Lozanne
N. S. Dixon
L. S. Fritz
J. M. Graybeal

W. P. Lowe
D. R. Lyons
L. Madison
E. R. Mapoles
G. P. Morgan

D. A. Rudman
A. J. Taylor
S. A. Trugman
J. C.-C. Tsai
G. A. Westenskow

J. R. Henderson
E. A. Hildum
W. T. Hill III
R. F. Hollman

M. A. Muntean
B. J. Neuhauser
S.-J. Oh

M. D. Williams
J. M. Wills
K.-P. Ziock

OTHER DEPARTMENTS

AERONAUTICS-ASTRONAUTICS

J. C. McDaniel

CIVIL ENGINEERING

L.-S. Gjaen

BIOPHYSICS

D. C. Torney

M.D. PROGRAM

S. L. Schmitt

APPENDIX - IV

IV. GRADUATE DEGREES CONFERRED

Doctor of Philosophy

N. M. Abbas	Chemical Engineering
I. M. Al-Khattat	Mechanical Engineering
P. C. Ariessohn	Mechanical Engineering
J. A. Aranovich	Materials Science and Engineering
M. A. Barteau	Chemical Engineering
J. A. Borsuk	Electrical Engineering
J. E. Bowers	Applied Physics
N. Bozorg-Grayeli	Materials Science and Engineering
J. F. Brady	Chemical Engineering
R. C. Bray	Electrical Engineering
A. N. Chu	Electrical Engineering
M. D. Cohen	Civil Engineering
B. H. W. S. de Jong	Geology
N. S. Dixon	Physics
M. D. Duncan	Applied Physics
J. A. Edighoffer	Applied Physics
M. J. Endemann	Applied Physics
R. D. Feldman	Applied Physics
P. D. Fitzgibbon	Chemical Engineering
P. Frank	Chemistry
S. Froyen	Applied Physics
S. H. Garofalini	Materials Science and Engineering
Y. S. Garud	Mechanical Engineering
C. R. Gochanour	Chemistry
R. B. Gold	Electrical Engineering
L. A. Gore	Applied Mechanics
A. Gupta	Chemistry
G. A. Hayward	Applied Physics
M. Hemami	Mechanical Engineering
W. T. Hill III	Physics
C. Ho	Materials Science and Engineering
Y. W. Hu	Applied Physics
C.-H. Hua	Applied Earth Sciences
D. J. Jackson	Physics
R. L. Jackson	Chemistry

GRADUATE DEGREES CONFERRED

Doctor of Philosophy (cont.)

J. M. Jasinsky	Chemistry
M. E. Kassner	Materials Science and Engineering
K. D. Keefer	Geology
D. B. Kimhi	Applied Physics
W. D. Kimura	Electrical Engineering
R. B. King	Mechanical Engineering
F. W. Kutzler	Chemistry
J. Kwo	Applied Physics
H. G. Lee	Electrical Engineering
S.-B. Lee	Mechanical Engineering
S.-C. Lee	Electrical Engineering
M. C. Leifer	Applied Physics
M. M. Mandurah	Electrical Engineering
F. K. Moghadam	Materials Science and Engineering
F. Mohammadi	Electrical Engineering
R. M. Nelson	Mechanical Engineering
Y. I. Nissim	Electrical Engineering
S.-Y. Oh	Electrical Engineering
W. C. Oliver	Materials Science and Engineering
W. A. Orr	Materials Science and Engineering
S. T. Oyama	Chemical Engineering
Y. Park	Applied Physics
B. Rezvani	Electrical Engineering
D. E. Richardson	Chemistry
S. T. Ruggiero	Applied Physics
M. P. Scott	Materials Science and Engineering
D. A. Seeburger	Geophysics
S. A. Shamma	Electrical Engineering
J. C. Sheppard	Electrical Engineering
J. C.-C. Tsai	Physics
H. C. Tuan	Electrical Engineering
R. B. van Dover	Applied Physics
J. C. Wei	Materials Science and Engineering
D. L. Weissman-Wenocur	Applied Physics
F. C. Wu	Electrical Engineering
A.-A. Ziaai-Moayyed	Materials Science and Engineering

GRADUATE DEGREES CONFERRED

Engineer

R. Maltiel	Materials Science and Engineering
R. O. Tatchyn	Electrical Engineering

Master of Science

A. I. Akinwande	Electrical Engineering
K. E. Alexander	Materials Science and Engineering
T. C. Anthony	Materials Science and Engineering
M. Bassan	Physics
C. M. Baylis	Materials Science and Engineering
S. Benjamin	Physics
J. C. Bravman	Materials Science and Engineering
M. S. Casey	Materials Science and Engineering
A.-M. Charvet(Fauchet)	Electrical Engineering
S. Chen	Electrical Engineering
A. W. M. Chow	Chemical Engineering
K. Chung	Mechanical Engineering
P. Chutikamontham	Materials Science and Engineering
K. L. Conway	Applied Physics
J. P. Doench	Materials Science and Engineering
M.-C. Dubourg	Materials Science and Engineering
J. C. Eakin, III	Materials Science and Engineering
A. Fischer-Colbrie	Materials Science and Engineering
J. A. Fournier	Materials Science and Engineering
G. F. Gallepos	Materials Science and Engineering
H. J. Groth	Materials Science and Engineering
G. F. Gwilliam III	Materials Science and Engineering
J. R. Henderson	Physics
K. P. Jackson	Electrical Engineering
S. W. Jorgensen	Chemical Engineering
A. Landauer	Materials Science and Engineering
Y.-S. Lee	Materials Science and Engineering
G. C. Lesh	Materials Science and Engineering
S. B. Libicki	Chemical Engineering
V. M. Ma	Chemical Engineering

GRADUATE DEGREES CONFERRED

Master of Science (cont.)

K. J. Mark	Materials Science and Engineering
M. J. C. Mayos	Materials Science and Engineering
P. A. McNally	Materials Science and Engineering
S. Morita	Materials Science and Engineering
B. C. Nguyen	Chemical Engineering
J. E. Nielsen	Materials Science and Engineering
V. Ponnaganti	Mechanical Engineering
S. A. Raza	Materials Science and Engineering
M. Riazat	Applied Physics
D. M. Rickey	Materials Science and Engineering
A. R. Selfridge	Electrical Engineering
J. E. Stein	Geophysics
C. Thompson	Materials Science and Engineering
D. M. Thornburg	Chemical Engineering
L. Volpe	Chemical Engineering
J. D. Walls	Geophysics
S. L. Westphal	Materials Science and Engineering
C. C. Williams	Electrical Engineering
M. D. Williams	Physics
C.-C. D. Wong	Materials Science and Engineering
Y. W. Yau	Applied Physics
K.-P. Ziock	Physics

NAME INDEX

V. NAME INDEX

Abbas, N. M. C*-219** E-426	Anderson, J. T. C-135	Avery, W. C-313
Abbati, I. C-339 D-399,402,420	Anderson, R. N. C-261	Ayter, S. C-68
Abernathy, C. C-76	Anson, F.C. D-405	Baer, R. L. C-210
Ahn, K.S. C-148,383 D-399	Anton, R. C-179 D-397,411	Baghdasarian, V. G. C-162
Akinwande, T. C-287	Antoniadis, D. A. D-414	Balakrishnan, K. C-227 D-400
Alden, T. H. C-246	Apted, M. J. C-103 D-403,424	Barbee, T. W. Jr. B-37,46 C-83,202,383 D-400,420
Alexander, J. A. D-418	Aranovich, J. C-112 D-399 E-426	Bardeleben, H. J. D-400
Alguard, M. J. D-399,401,418	Ariessohn, P. C. C-132 D-399 E-426	Barfknecht, A. T. C-100
Al-Khattat, I. M. B-58 C-214 E-426	Aspandiar, R. F. C-202	Barnett, D. M. 3, B-58 C-73
Allcock, H. R. C-76	Auld, B. A. B-3 C-68,148 D-399,419	Barrett, J. H. D-399
Allen, L. H. C-83	Avalos-Borja, M. C-179 D-399	Barteau, M. A. C-219 D-400 E-426
Altkorn, R. I. C-396		
Andersen, H. C. B-37,39 D-407		

*Section

**Page

B - Thrust Research Programs

C - Individual Research Programs

D - Publications

E - Doctoral Dissertations

Bartholomeusz, P. J. C-261	Benson, J. E. C-92	Bott, S. E. C-282
Bartman, E. C-123	Benson, S. V. D-425	Bouchet, D. B-37,50 D-415
Barton, R. W. C-186,287,334,383 D-420	Benziger, J. B. D-401	Boudart, M. B-32 C-92 D-402,414
Bartoszek, F. E. C-396	Berclaz, T. D-401	Boukamp, B. A. C-202 D-402
Bassan, M. C-135	Berding, M. A. C-130,199	Bourell, D. L. D-421
Bates, C. W. Jr. C-76 D-400,401,408	Berg, J. D-413	Bowers, J. E. C-202 E-426
Baumrind, N. L. C-383	Bergh, R. A. C-309 D-401	Bowker, M. A. D-400
Beasley, M. R. B-37 C-83 D-401,414,418,420 424	Berman, B. L. D-399,401,418	Boxer, S. G. C-96 D-402,403,415,425
Beckworth, S. K. C-374,376	Bienenstock, A. I. B-37,40 C-89	Boyers, D. G. C-383
Belmont, J. A. C-123	Binns, C. C-339	Brady, J. R. E-426
Bencosme, C. S. C-123 D-405	Bloom, S. D. D-399,401,418	Braicovich, L. C-339 D-399,402,420
Bending, S. J. C-83 D-418	Bloomfield, L. A. C-302 D-405	Brauman, J. E. C-100 D-402,405,412,418, 420,425
Benjamin, S. C-135	Blum, W. C-246 D-422	Bravman, J. C. C-334 D-422
Bennett, K. E. C-120 D-401	Boek, H. D. C-103	Bray, R. C. D-402 E-426
Bennett, P. A. C-210	Borghard, W. G. C-92	Brennan, S. M. C-89 D-402
Bennett, S. D. B-3 C-210	Borshchevsky, A. D-401,423	
	Borsuk, J. A. C-374 D-402 E-426	

Brian, A. A. C-227	Carey, K. W. C-179	Cheng, Y. L. C-300
Brinkman, R. C. D-404	Carlson, N. W. C-302	Chiang, C. C. C-225 D-417
Bronner, C. C-287	Carranza, R. A. C-148 D-399	Chidsey, C. E. C-96
Brothers, P. J. C-123	Carriger, R. C-313	Chodorow, M. C-309
Brown, G. E. Jr. C-103 D-402,403,405,411, 422,424	Carter, W. L. B-37,46 D-404	Chong, A. O. D-405
Browne, D. A. C-126	Cartwright, G. S. C-227	Chou, C. H. C-210 D-404
Bube, R. H. C-112 D-399,403,410,412, 419,424	Casey, M. S. C-112	Chow, A. B-31
Buchanan, D. N. E. D-401	Cass, T. R. D-413	Christel, L. A. C-166 D-404,417
Buckingham, M. J. C-403	Celaschi, S. B-37,46	Chu, A. N. C-253 D-404 E-426
Bucks, R. R. C-96 D-402,403	Challinger, K. D. D-404	
Buhr, J. D. D-403	Chan, K. S. C-235	Chung, K. B-58 C-214
Buskirk, R. F. D-404	Chang, C. H. D-413	Chye, P. W. D-422,423
Byer, R. L. C-120,148 D-401,403,406,408, 409,418,425	Chang, S. C. C-367 D-423	Clements, K. E. D-401
	Chen, D. C-287	Co, M. S. C-199
	Chen, L.-C. D-425	Cohen, M. D. C-298 E-426
Cabrera, B. C-135	Chen, L.-T. H. B-17	Collins, T. J. C-123 D-405
Cafiso, D. S. C-227	Chen, S. C-287	
Calhoun, J. D-402	Cheng, W. C. C-92	Collman, J. P. C-123 D-405

Conradson, S. D. C-199	Deal, M. G. C-367	Dixon, N. S. C-174 E-427
Conway, K. L. C-166	Dehmer, J. L. D-419	Doench, J. P. C-202
Cook, C. F. D-405	de Jesus, S. M. III B-58 C-313	Doniach, S. C-126,130,199 D-406,413,415,416
Cooper, A. D. D-400	de Jong, B. H. W. S. D-405 E-426	Drzaic, P. S. C-100
Corl, P. D. C-210	Deline, V. R. D-417	Duff, B. W. C-300
Cotter, N. E. C-395	Dell'Oca, C. J. D-413	Duncan, M. D. C-120 D-403 E-427
Couillaud, B. C-302 D-405,410,414,422	de Lozanne, A. J. C-83 D-425	Dutton, R. W. C-287 D-414
Cramer, S. P. D-413	De Mattei, R. C. B-17 C-148 D-406,421	Eades, W. D. C-374
Crane, R. A. C-374,376	Denisevich, P. J. D-405	Early, S. R. B-37,46
Crites, R. C-313	Deublein, G. C-202	Earthman, J. C. C-246
Cutler, C. C. C-309 D-405	Deutsch, C. C-126	Eberspacher, C. C-112
Dabkiewicz, P. C-302	Dibble, W. E. C-383 D-406	Ediger, M. D. C-145
Dalla Betta, R. A. C-92	Digonnet, M. C-148,309	Edighoffer, J. A. C-253 D-406 E-427
Dameron, D. H. B-17	Di Iorio, M. S. C-83	Eggleston, J. M. III C-120 D-403
Datz, S. D-399,401,418	Dill, D. D-419	Eglash, S. J. C-339
Deacon, D. A. C-135	Dill, K. A. C-157 D-406	
Deal, B. E. C-287 D-420		

Eiselstein, L. E. C-313	Fauchet, P. M. C-327	Foley, M. E. C-379
Elwell, D. C-148,202,383 D-399,406,419	Fayer, M. D. C-145 D-409,415,417	Foner, S. D-418
Endemann, M. J. C-120 D-404,406 E-427	Fearon, D. T. D-418	Fortmann, C. M. C-112
Erman, B. C-157 D-406,407	Feigelson, R. S. B-17 C-148,202,383 D-399,400,401,404, 406,407,419,424	Fouquet, J. E. C-329
Eustis, R. H. C-132 D-399	Fejer, M. M. C-148	Fox, D. C. D-405
Evans, C. A. D-417	Feldman, R. D. B-37,46 D-407 E-427	Fox, J. R. B-37,39 D-407
Everitt, C. W. F. C-135	Fenn, P. M. C-103	Franciosi, A. D-399
Everson, R. C. C-92	Fesler, K. A. B-17 C-309 D-421	Frank, C. W. B-17,28 C-159 D-407,408,420,421
Evitt, E. R. C-123 D-405	Finman, P. F. C-253	Frank, P. E-427
Ewell, G. J. D-415	Fischer-Colbrie, A. B-37,40	Fredricksen, H. P. D-407
Fahrenbruch, A. L. C-112,148 D-399	Fitzgibbon, P. D. C-159 E-427	Frey, T. E. C-227
Fair, J. D-407	Flamberg, A. C-282	Fritz, L. S. C-174
Fairbank, W. M. C-135 D-419,420,425	Flamberg, P. C-379	Frommeyer, G. C-313
Fairclough, R. A. C-130,199	Flory, P. J. C-157 D-406,407,412,415 420,424,425	Froyen, S. B-32 C-176 D-407 E-427
Fauchet, A. M. C-253	Foley, D. C-126	Fuchs, H. O. C-162
		Fuchs, K. P. C-246

Fuentes-Samaniego, R. D-407,408	Gelles, R. G. B-28 D-408	Gore, L. A. C-73 E-427
Fujita, I. D-403	Gerhardt, H. C-302 D-412	Grabow, M. H. B-37,39
Fuller, G. G. B-17,31 C-164 D-408	Geselowitz, D. A. C-379	Gran, J. K. C-214
Fuoss, P. H. B-37,40	Gibbons, J. F. C-166,287 D-404,408,413,416, 417,421	Graybeal, J. M. C-83
Gaeta, C. C-309	Gibeling, J. C. C-246 D-408	Grayeli, N. C-325 D-409,422 E-426
Galan, L. D-400,408	Giffard, R. P. D-411	Green, J. B. C-210
Gan, S. T. B-17	Gilman, P. S. D-408	Gregory, J. K. C-246
Garber, J. F. C-202	Gittleman, J. C-339	Greiner, M. E. C-166
Garel, T. C-126	Giuliani, G. D-408,409,418	Gupta, A. D-409 E-427
Garofalini, S. D-408,416 E-427	Gjaen, C. L. C-68	Gür, T. M. D-409
Garud, Y. S. C-162 E-427	Gochanour, C. R. C-145 D-409,415 E-427	Gustafson, E. K. C-120
Gashgari, M. A. B-28	Goffe, R. A. D-409	Gutfreund, H. D-409
Gasser, R. A. C-367	Gold, R. B. C-166 D-417 E-427	Hackert, M. C-309
Gdowski, G. E. C-219 D-408	Goldstein, B. C-103	Hafeman, D. G. C-227 D-409,418
Geballe, T. H. B-37,46 C-148 D-404,407,408,413	Golmayo, M. D. D-399	Hagane, T. D-421
Geller, T. D-400	Goltzené, A. D-400	Haines, W. G. D-410

Halicioglu, T. C-383 D-408	Henderson, J. R. C-135	Hochella, M. F. Jr. C-103 D-411
Hameson, G. B. D-405	Henesian, M. A. C-120	Hodgson, K. O. C-130,199 D-413,415
Hammershoi, A. C-379	Henshall, G. A. C-235	Hollenhorst, J. N. D-411
Hammond, R. H. B-37,46 C-83 D-407,408,418	Heritier, J. W. C-329	Holliger, C. C-300
Hanna, S. S. C-174	Herring, C. C-197 D-403,411	Hollman, R. F. C-217
Hansch, T. W. C-302 D-405,410,412,414, 422,425	Herrmann, A. G. B-3	Holstein, W. L. C-92
Harrison, W. A. B-32 C-176 D-410,419	Herrmann, G. B-3 D-411,413	Hong, J. D. D-421
Hartwig, P. D-410,420,425	Heshmatpour, B. D-411	Howard, F. D. IV C-227
Hauser, U. C-217	Hess, B. A. Jr. D-420	Howard, R. E. D-424
Hayward, G. A. E-427	Hessenbruch, A. C-103	Hu, Y. W. E-428
Hecht, M. H. C-339	Hibbs, M. K. D-411	Hua, C. H. C-261,313 D-411 E-428
Hegedus, L. S. D-405	Hiberty, P. C. D-412,425	Huber, W. C-112
Heinemann, K. C-179 D-399,411,419	Hildum, E. A. C-302	Huberman, B. A. C-126 D-411
Hellman, F. B-37,46	Hill, W. T. III C-302 E-428	Huggins, R. A. C-148,202,392 D-402,409,412,413, 419,424,425
Helms, C. R. C-186,287,334 D-405,411,415,420	Hino, I. D-422	Hughes, D. A. C-246
Hemami, M. E-428	Ho, C. E-428	Hull, G. W. Jr. D-404
	Ho, C. P. C-287 D-420	

Hulm, J. K. D-408	Jackson, R. L. C-100 D-412 E-428	Kang, X.-H. C-92
Hummel, J. P. D-406,411,420	Jaeger, R. D-402	Kao, C. Y. C-76,267
Hung, Y. D-412	Jameson, G. B. D-405	Kaplan, D. D-415
Ibers, J. A. D-405	Jan, Z. S. D-412	Kassner, M. E. C-235 D-421 E-428
Ichikawa, S. C-92	Janousek, B. K. D-412	Keefer, K. D. C-103 D-405 E-428
Iglesia, E. C-92	Jasinski, J. M. C-100 D-412,420 E-428	Keith, D. L. D-400
Ilan, Y. C-379	Jew, K. G. C-267	Keskinen, M. D-411
Ilić, D. B. D-409	Johansson, L. I. C-339	Ketruch, P. I. D-423
Inloes, D. S. C-300	Johnson, S. D-412	Khuri-Yakub, B. T. B-3 C-210 D-404,419
Iranmanesh, A. A. C-276	Jones, K. M. C-302	Kihlstrom, K. E. B-37,46
Irvine, P. A. C-157	Joo, S.-K. C-202	Kim, K. S. C-286
Itoh, T. D-421	Jordan, M. T. C-76	Kim, Y. S. C-76
Iverson, B. D-405	Jorgensen, S. C-219	Kimhi, D. B. B-37,46 D-413 E-428
Jackson, C. W. C-73	Jupiter, P. J. C-339	Kimura, W. D. C-253 D-406 E-428
Jackson, D. J. C-302 D-412 E-428	Kaiser, G. C-135	King, R. B. B-3 D-413 E-428
Jackson, K. H. D-419	Kamins, T. I. C-287 D-413,415	

Kino, G. S. B-3 C-210 D-404,409,413,419, 422	Kreuer, K. D-413	Lamereaux, R. C-76
Kircher, C. J. C-401	Krieger, G. C-374	Landauer, A. C-339
Kisker, D. C-367 D-413	Kruger, C. H. C-132	Landstrass, M. I. C-267
Knapp, J. C-300	Kubiak, G. D. C-396	Larson, L. C-179
Ko, E. I. D-400,401,413	Kuki, A. C-96	Lawler, J. E. C-302 D-405,414,422
Kobrin, A. R. C-202	Kum, D. W. C-313	Leclerq, G. D-414
Koch, R. D-402	Kump, M. R. C-287	Lee, C.-T. C-148
Koenig, F. C-120	Kung, W.-J. D-412	Lee, E. H. B-58 C-214 D-414,415
Koester, J. K. C-132	Kunkel, H. C-68	Lee, H. G. E-429
Kolner, B. C-309	Kutlu, E. C-287	Lee, H. W. C-145 D-417
Konai, Y. D-405	Kutzler, F. W. C-130,199 D-413,416 E-428	Lee, J. C-219
Kong, E. C-179	Kwark, Y. C-376 D-413	Lee, J. J. C-164
Kortwright, J. B-37,40	Kway, W. L. C-148 D-404	Lee, K. F. C-166 D-413,416,421
Kosydar, K. M. C-123	Kwo, J. B-37,46 D-408,413,414,418 E-428	Lee, L. S. C-302
Koto, K. D-413		Lee, M. C. Y. C-202
Koval, C. D-405	Ladas, S. D-414	Lee, S. C-219
Kreh, R. P. C-123	Laderman, S. B-37,40	Lee, S.-B. E-429

Lee, S. C. C-267 D-414 E-429	Liou, J. G. D-411	Madonik, A. M. C-123
Lee, Y. S. B-37,53 C-367	Lipa, J. A. C-135	Mael, D. J. B-37,46
Lefevre, H. C-309 D-401	Little, W. A. C-217 D-409	Magee, T. J. D-416,417,421
Leifer, M. C. C-135 E-429	Lok, B. K. C-300	Maier, K. R. C-282
Lemley, K. V. C-300	Long, S. Y. C-120	Makinouchi, A. C-214
Lesh, G. C. D-402	Lopez-Otero, A. C-112	Mallett, R. L. B-58 C-214
Levy, M. D-407	Loring, R. F. C-145	Malloy, K. J. C-267
Lew, P. W. C-186	Lowe, T. C. C-235	Mandelkern, D. B-17
Liang, K. K. C-210 D-404	Lowe, W. P. B-37,46	Mandurah, M. M. C-287 D-415 E-429
Libicki, S. B. C-300	Lubarda, V. D-415	Mapoles, E. R. C-135
Lietoila, A. C-166 D-408,417	Lutz, D. R. C-145 D-415,417	Marin, G. C-92
Lin, A. M. D-414	Lye, R. C. C-130,199 D-415	Mark, A. J. C-202
Lin, J. H. D-421	Lyons, D. R. C-302 D-410	Mark, K. J. C-367
Lindau, I. C-126,339 D-399,402,414,416 418,420,421,422 423	Madey, J. M. C-135	Marks, J. C-100
Ling, D. T. D-414,416,422	Madison, L. C-145 D-417	Marrocco, M. D-405
Linville, J. G. B-17	Madix, R. J. B-32 C-219 D-400,401,407,408 412,413,421,422 424,425	Marshall, A. F. B-37,50 D-400,415

Martinez, L.
C-246
D-415

Mason, D. M.
C-225
D-409,417

Massoud, H. Z.
C-287

Matheson, R. R.
D-415

McAshan, M. S.
C-135

McConnell, H. M.
C-227
D-400,401,409,418,
419,423,424

McCord, E. F.
C-96
D-415

McDaniel, J. C.
C-120

McDonald, M. A.
C-92

McLean, W. L.
D-424

McMeeking, R. M.
D-414

McNiff, E. J.
D-418

Mecartney, M. S.
D-415

Mehdi, S. Q.
C-227

Mei, L.
C-287

Meier, K.
D-405

Meindl, J. D.
C-287

Meitzner, G.
C-92

Melberg, M.
C-300

Meng, G.-Y.
C-367

Meyer, F. K.
C-100

Michaels, A. S.
B-17

Michal, G. M.
D-415,416,422

Michelson, P. F.
C-135

Michielsen, S. P.
C-282

Miller, A. K.
B-58
C-162,235
D-404,416,420,421

Miller, J. N.
D-402,414,416

Miller, R. J. D.
C-145

Mills, M. J.
C-246

Minagawa, S.
D-416

Misemer, D. K.
D-413,416

Moberly, W. J.
C-313

Modlin, D. N.
C-383

Moghadam, F. K.
C-367
D-416
E-429

Mohammadi, F.
C-287
E-429

Moine, P.
D-415,416

Moog, R.
C-96

Mooney, J. B.
C-76

Morgan, G. P.
C-302

Morgen, P.
C-339

Moslehi, B.
C-309

Moylan, C. R.
C-100

Mruzik, M. R.
D-416

Muennemann, F. G.
C-68
D-399,419

Mulac, W. A.
D-423

Mylroie, S.
D-404

Nagel, L. E.
C-383

Natoli, C. R.
D-413,416

Nelson, D. V.
B-3
C-162,244
D-416

Nelson, K. A.
C-145
D-415,417

Nelson, K. M. C-76	Oesterlin, P. C-120 D-403	Oyama, T. B-32 C-92,313 D-402,421 E-429
Nelson, R. M. C-132 E-429	Oh, S. J. C-126,339	Ozawa, T. C-123
Nelson, W. H. C-282	Oh, S. Y. C-287 E-429	
Netzel, T. L. D-403	Ohta, T. D-418	Pacey, A. B-32 C-219
Neuhauser, B. J. C-135	Okade, M. D-421	Pannetier, B. C-83
Newton, S. A. C-309 D-405	Oliver, N. H. C-282	Pantell, R. H. C-253 D-399,404,406,418, 424,425
Ng, C. Y. C-112	Oliver, W. C. C-246 D-417,422 E-429	Park, Y. K. C-120 D-404,408,409,418 E-429
Nguyen, B. C-225	Olson, R. W. C-145 D-417	Parks, G. A. C-258
Nieh, T. G. D-417	Ong, B. G. C-225 D-417	Parlee, N. A. D. C-261 D-411
Nielson, J. C-112	Opfer, J. E. D-425	Parr, A. C. D-419
Nishimura, K. C-112	Opyd, W. G. C-166	Pate, B. B. C-339 D-418,421
Nissim, Y. I. C-166 D-408,417 E-429	Orlando, T. P. C-83 D-414,418	Patterson, F. G. C-145 D-417
Nix, W. D. C-246 D-407,408,415,417, 422	Ormond, R. D-416,417	Pavlath, G. A. C-309
Norberg, J. C. D-417	Orr, W. A. C-112 E-429	Pearson, G. L. C-267 D-414
Oakley, R. T. D-405	Orwoll, R. A. C-157	Pease, R. F. W. C-276 D-413,424
Ocken, H. D-416	Outka, D. A. C-219	

Pecora, R. C-282 D-425	Piekarczyk, W. D-425	Rabenau, A. C-410,413,425
Pellerite, M. J. C-100 D-412,418	Piestrup, M. A. C-253 D-404,406	Raistrick, I. D. C-202,392 D-409,419
Peng, J. D-421	Pirouz, P. D-422	Ramsay, D. C-174
Perez, M. A. B-37,46	Piziali, R. L. C-286	Rand, S. C. C-302
Perino, S. C. C-186	Plavsic, M. C-157 D-420	Rao, G. M. C-148 D-419
Perry, D. S. D-409	Plummer, J. D. C-287	Raybuck, S. A. C-123
Persson, I. C-379	Pohl, D. C. C-258	Raymakers, R. J. C-148
Peterson, D. K. C-210	Polasko, K. J. C-276	Raza, S. A. C-76
Petrie, M. C-313	Poliakoff, E. D. D-419	Razouk, R. R. D-420
Petro, W. G. C-339	Ponce, F. A. C-112 D-419,422	Racktenwald, D. J. D-419
Pettman, R. B. C-123 D-405	Poon, S. J. B-37,46 D-404,418	Reed, K. J. D-412
Petty, H. R. C-227 D-418	Poppa, H. C-179 D-399,411,419	Rek, Z. U. C-199
Phillips, J. C. D-415	Poris, J. C-202 D-419	Ren, S.-Y. C-176 D-419
Phillips, J. D. C-135	Pound, G. M. D-407,408,416	Rennagel, H. C-396
Philo, J. S. D-419	Prutton, M. C-179	Resch, M. T. B-3 D-419
Phizackerley, R. P. C-199		Retner, C. T. D-420
Pianetta, P. D-414	Quate, C. F. B-3 D-402	Rezvani, B. E-429

Riazlat, M. B-3 C-68	Ruano, O. A. C-313 D-421	Schawlow, A. L. C-302 D-410
Richards, C. W. C-298	Rubin, C. C-313	Schmidt, C. G. D-420
Richardson, D. E. C-379 E-430	Rubin, K. R. C-235	Schmitt, S. C-300
Rigby, K. W. C-135	Rudman, D. A. C-83 D-420	Schmittou, E. R. D-405
Rivier, M. C-202	Rudo, K. D-420	Schulz, H. D-413
Roberts, K. J. D-406	Rugar, D. B-3	Schwab, C. D-400
Robertson, C. R. C-300	Ruggiero, S. T. C-83 D-420 E-430	Schwartz, S. A. D-416
Robinson, K. E. C-135	Rynard, C. M. C-100 D-420	Schwarz, S. D-402,420
Roelofs, M. G. C-96		Schwettman, H. A. C-135
Rose, E. D-405		Scott, J. C-300
Rosenfeld, R. N. D-420	Saiz, E. D-420	Scott, M. P. B-58 C-73 E-430
Rossi, G. C-339 D-420	Salomon, K. E. C-100	Scott, N. C-379
Rouse, J. W. C-186,287 D-420	Salvo, H. L. D-407	Scott, R. A. C-199 D-413
Route, R. K. B-17 C-148 D-424	Sanchez, J. C-92	Seaward, K. L. C-383
Rowe, J. E. D-402	Saraswat, K. C. C-287 D-415	Seeburger, D. A. E-430
Rowland, S. C. B-37,40	Sato, T. C-210	Seki, H. C-367
	Schaad, L. J. D-420	Self, S. A. D-399
	Schaeffer, H. F. III D-425	

Selfridge, A. R.
C-210

Semerak, S. N.
B-28
D-420

Sen, J. P.
C-379

Sessler, J. L.
C-123
D-405

Sexton, B.
D-421

Shaikh, N.
B-3

Shamma, S. A.
C-395
E-430

Shaw, H. J.
B-17
C-148,309
D-401,405,421

Shek, M. L.
C-339
D-416,421

Sheppard, J. C.
C-253
E-430

Sherby, O. D.
B-58
C-313
D-421

Shibata, T.
D-421

Shigley, J. E.
C-103
D-422

Shinde, S. L.
D-415

Shyne, J. C.
B-3
C-325
D-409,419,422

Siegel, A.
C-302
D-405,410,414,422

Siegman, A. E.
C-327,329,332

Sigmon, T. W.
D-417

Silberman, J.
C-339

Silverman, E. M.
D-422

Simkins, M. M.
C-148
D-406

Sinclair, R.
B-37,50
C-335
D-411,415,416,419,
422

Singer, R.
D-422

Skeath, P. R.
C-339
D-399,402,422,423

Slater, J.
C-235

Slivinsky, S.
C-261

Smith, C.
C-309

Smith, J. D.
C-246

Smith, L. M.
C-227
D-418,423

Smith, W. J.
C-300

Snyder, B. C.
C-313

Socie, D. F.
D-416

Sorin, W.
C-309

Spicer, W. E.
B-32
C-339
D-399,402,414,416
418,420,421,422
423

Stanbury, D. M.
D-423

Stanke, F. E.
B-3
C-210
D-409

Stanton, S. G.
C-282

Stearns, D. G.
B-37,40
C-210

Steeds, J. W.
D-415

Steele, C. R.
B-3

Stefan, P. M.
B-32
C-339
D-414,416,421

Stein, C. A.
D-423

Stephens, J. J. C-246	Swent, R. L. C-253 D-399,401,418,424	Thornton, R. C-210
Stephenson, G. B. B-37,40	Swirhun, S. E. C-374	Thorpe, T. P. C-112
Stevens, P. A. C-176,219		Tien, J. J. C-210 D-219
Stevenson, D. A. B-37,53 C-261,367 D-400,411,413,416, 423	Taber, M. A. C-135 Taber, R. C. C-135	Tiller, W. A. C-148,287,383 D-406,414
Stöhr, J. C-89 D-402	Talvacchio, J. J. B-37,46	Tipton, S. C-244
Stokes, L. C-309	Tan, M. C-68	Tokizane, M. D-421
Stringer, J. C-367	Tanaka, T. B-58 C-235	Tolf, E. G. C-73
Stroud, R. C-130	Tasooji, A. C-235 D-416	Trebino, F. P. C-332
Stultz, T. C-166	Tatchyn, R. O. C-339	Tripathi, V. S. C-258
Stuve, E. M. C-219	Taube, H. C-379 D-403,412,423	Trugman, S. A. C-126
Su, C. Y. C-339 D-399,402,422,423	Taubenblatt, M. A. C-186	Trutna, W. R. D-424
Suda, T. C-112	Taylor, A. J. C-302	Tsai, J. C. C-302 E-430
Sullivan, J. C. D-423	Taylor, C. M. D-405	Tuan, H. C. C-210 E-430
Swaminathan, B. C-287	Thathachari, Y. T. C-383	Tuckerman, D. B. C-276 D-424
Swanson, R. M. C-374,376 D-402,413	Thomas, J. W. B-28	Tumas, W. C-100
Swenson, L. W. Jr. C-286	Thornberg, D. M. C-219	Turneure, J. P. C-135

Uekita, M. C-76	Wang, Z.-Y. C-302 D-410	Wertheim, G. K. C-76 D-401
Unternahrer, S. C-120	Wann, G. S. C-123	Wertheimer, T. B. B-58 C-214
van Attekum, P. M. Th.M. D-401	Warburton, W. K. B-37,40	Werthen, J. G. C-112
van Dover, R. B. D-424 E-430	Ware, D. C-379	Westenskow, G. A. C-135
Viescas, A. J. C-339	Warner, M. D-424	Westphal, S. L. C-383
Volpe, L. C-92	Watkins, K. J. B-17	Wetmore, R. W. D-425
von Tscharner, V. D-409,424	Waychunas, G. A. B-37,56 C-103 D-403,424	White, R. L. C-395
	Weber, R. S. C-92	Wichelhaus, W. D-410
Wachs, I. E. D-424	Webster, C. R. D-420,424	Wikswow, J. P. Jr. D-420,425
Wadsworth, J. C-313 D-421	Wei, J. C. C-246 E-430	Williams, M. D. C-339
Wakita, A. C-166	Weinstein, D. G. B-17 C-309 D-420	Wills, J. M. B-32 C-176
Walmsley, R. G. B-37,53 C-367 D-400,415	Weis, R. M. C-227 D-423	Winkler, K. W. D-403
Wang, C.-C. C-282	Weissman-Wenocur, D. L. C-339 D-414,416,421 E-430	Winslow, D. K. D-399,419
Wang, D. Y. C-253 D-406	Wen, C. J. D-424,425	Wishart, J. C-379
Wang, F. C. C-112,148 D-424	Weppner, W. C-202,392 D-410,413,420,425	Wolfe, C. R. C-217
Wang, J. S. C-246		Wolfe, D. C. Jr. C-120
		Wong, C. C. C-112

Woo, L. K. C-123	Yie, J. E. C-92	Zitelli, L. T. B-17 C-309 D-421
Worden, P. W. Jr. C-436	Ying, D. H. D-425	
Wright, J. C. C-300	Yoneda, T. C-92	
Wright, K. A. C-96 D-425	Yoon, D. Y. D-425	
Wu, D.-C. C-157	Young, E. M. C-383	
Wu, F. C. C-166 D-408 E-430	Youngquist, R. C. C-197	
Wu, M. Y. C-313	Yu, K. S. C-179	
	Yuen, J. L. C-246	
Xia, H. R. C-302 D-425	Zakowicz, W. D-425	
	Zambre, Y. B. C-302	
Yamashita, T. D-416,419,422	Zare, R. N. C-396 D-409,419,420,424	
Yan, G.-Y. C-302 D-410	Zebrowski, B. E. C-282	
Yaney, D. C-313	Zero, K. M. C-282 D-425	
Yarim-Agaev, Y. C-157	Zhang, G. C-92	
Yarita, I. C-214	Ziaai-Moayyed, A. A. C-235 D-416 E-430	
Yau, Y. W. C-276		
Yeh, A. C-379	Ziack, K.-P. C-217	
Yeh, S. C-300		

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SUPPLEMENTARY

INFORMATION

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- [7] Y. I. Nissim and J. F. Gibbons, "CW Laser-Assisted Diffusion and Activation of Sn in GaAs from a Spin-on $\text{SnO}_2/\text{SiO}_2$ Source," presented at the E.C.S. Meeting, St. Louis (May 1980).
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- [9] Y. I. Nissim, J. F. Gibbons, R. B. Gold and D. M. Dobkin, "CW Laser-Assisted Diffusion of Tin in GaAs for Non-Alloyed Ohmic Contacts," presented at the E.C.S. Meeting, Hollywood, Florida (October 1980).
- [10] Y. I. Nissim, L. A. Christel, T. W. Sigmon, J. F. Gibbons, T. J. Magee and R. Ormond, "Solid Phase Epitaxial Regrowth in Ion Implanted GaAs" accepted in Appl. Phys. Lett.
- [11] Y. I. Nissim, L. A. Christel, T. W. Sigmon, J. F. Gibbons, T. J. Magee and R. Ormond, "Solid Phase Epitaxial Regrowth in Ion Implanted GaAs" to be presented in E.M.C. Meeting, Santa Barbara (June 1981).

(5) Computer Modeling of the Temperature Rise and Carrier Concentration Induced in Si by Pulsed Lasers

Graduate Student: Arto Lietoila

Objective: To study the mechanism of pulsed laser annealing of implanted Si; i.e., to find out whether the annealing involves melting of the sample surface, or whether the so-called "plasma annealing" occurs.

Results: A computer model was developed which simultaneously solves the partial differential (diffusion) equation for lattice temperature, carrier temperature and carrier concentration produced in Si by pulsed lasers. For nanosecond pulses, the model predicts that the melting temperature of Si is reached with pulse energies similar to those required to cause the experimentally observed enhanced reflectivity (~ 70%) of the sample surface. Thus it is concluded that the

mechanism of nanosecond pulse annealing is melting and resolidification.

For picosecond pulses, the model predicts that the pulse energy is at first stored in the hot carrier system. However, the carriers relax their energy after the pulse, and the melting temperature of Si would still be reached with pulse energies which have been experimentally observed to cause annealing.

(6) Study of the CW Laser Induced Solid Phase Epitaxial Regrowth of Amorphous Si

Graduate Student: Arto Lietoila

Objective: To measure the rate of solid phase epitaxial regrowth of self-implantation amorphized Si under typical laser annealing conditions to study the obstructed regrowth of thick amorphous layers.

Results: The rate of regrowth was measured both by determining the time required to regrow a thin amorphous layer ($\sim 1000 \text{ \AA}$), and by observing partial regrowth of thick ($\sim 4000 \text{ \AA}$) layers. In both cases, it was found that the rate of regrowth is enhanced by an order of magnitude compared with extrapolated low temperature data.

It was also found that thick amorphous layers could not be completely regrown with the laser: formation of polycrystalline Si will stop the regrowth after about 2500-3000 \AA have grown. Doping of the amorphous layer does not markedly increase the amount of maximum regrowth. The results obtained would indicate that nucleation and growth of polysilicon takes place uniformly throughout the amorphous material, rather than starting from the sample surface.